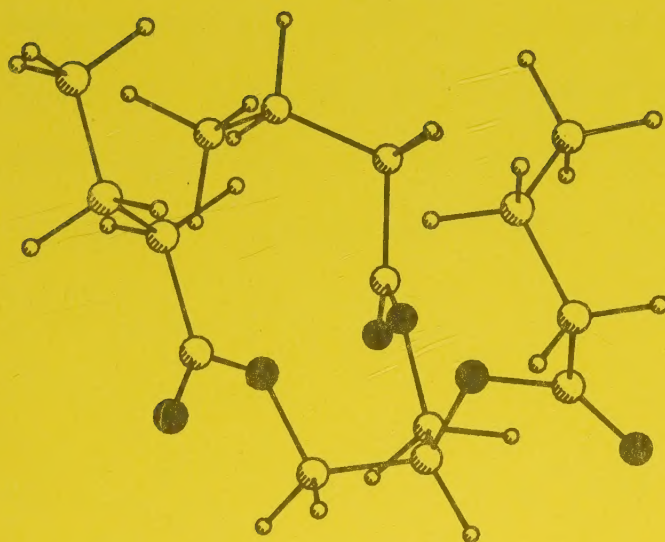
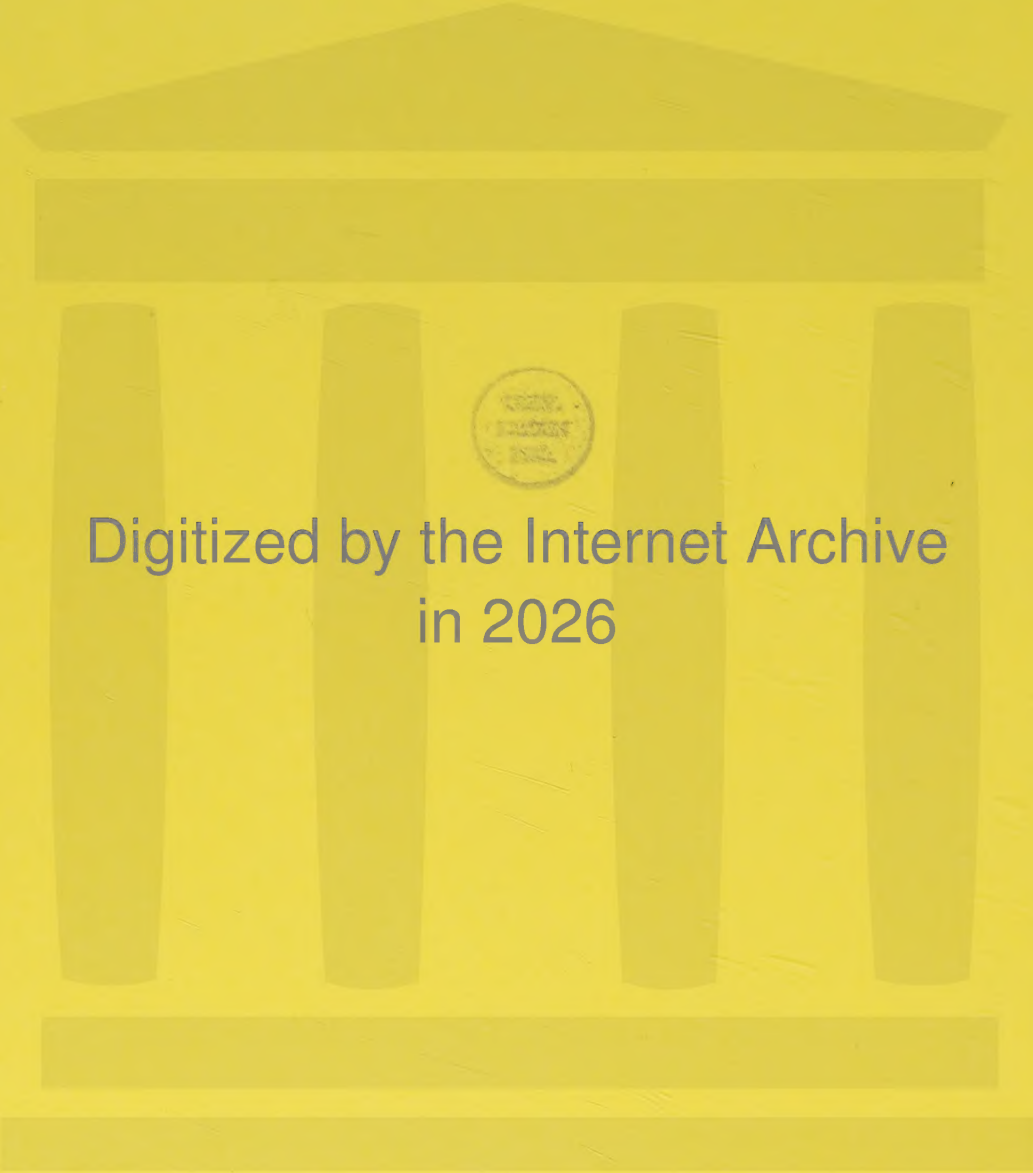


A THERMOCHEMICAL STUDY OF INTERACTIONS BETWEEN WATER AND SOME HYDROCARBONS, ALCOHOLS AND ESTERS

Sven-Ove Nilsson



Lund 1986



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by

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"When you can measure what you are speaking about and express it in numbers, you know something about it; and when you cannot express it in numbers, your knowledge is of meagre and unsatisfactory kind."

- Lord Kelvin

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Abstract Flow microcalorimetric vessels for dissolution of easily or slightly soluble liquids and slightly soluble solids in water have been designed and tested. Enthalpy of solution measurements of n-alkan-1-ols (C_1 to C_8) and some mono-, di- and triesters in water have been performed to infinitely dilute aqueous solution at different temperatures. Partial molar heat capacities are derived from the enthalpy temperature dependence. These results are shown to be highly additive for all compounds except for glycerol tributanoate. The deviation indicates hydrophobic intermolecular interactions between the alkyl chains. Calorimetric dissolution measurements of water in some hydrocarbons, alcohols and esters have also been performed. The enthalpy of solution values are indentical for the n-alkanes (C_7-C_{12}) and a heat capacity change close to zero is obtained. This led to an equation which describes the water solubility in n-alkanes as a function of the number of carbon atoms and the temperature .		
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Signature Sven-Ove Nilsson

Date March 10, 1986

This thesis is based on the following papers, which are referred to by the Roman numerals I-VI.

I. Nilsson, S.-O.; Wadsö, I.

A flow-microcalorimetric vessel for solution of small quantities of easily or slightly soluble liquids. Solution of benzene in water at 298.15 K.

J. Chem. Thermodynamics 1984, 16, 317.

II. Nilsson, S.-O.; Wadsö, I.

A flow microcalorimetric vessel for solution of slightly soluble solids.

J. Chem. Thermodynamics: submitted.

III. Hallén, D.; Nilsson, S.-O.; Rothschild, W.; Wadsö, I.

Enthalpies and heat capacities for n-alkan-1-ols in H_2O and D_2O .

J. Chem. Thermodynamics: in press.

IV. Nilsson, S.-O.; Wadsö, I.

Thermodynamic properties of some mono-, di- and tri-esters.

Enthalpies of solution in water at 288.15 to 318.15 K and enthalpies of vaporization and heat capacities at 298.15 K.

J. Chem. Thermodynamics: in press.

V. Nilsson, S.-O.

Enthalpies of solution of water in benzene and in some n-alkanes.

J. Chem. Thermodynamics: in press.

VI. Nilsson, S.-O.

Partial molar enthalpies of solution of water in some n-alkan-1-ols and esters at 298.15 and 308.15 K.

J. Chem. Thermodynamics: submitted.

1. INTRODUCTION

Practically all chemical and physical processes are accompanied by heat effects. Measurement of heat effects, calorimetry, was first reported towards the end of the eighteenth century (Armstrong, 1964)⁽¹⁾ and since that time has contributed invaluable data to practicing chemists and to the development and testing of theories of chemical interactions.

Calorimetry on biological systems (biocalorimetry) seems to be as old as calorimetry itself. In 1780 Crawford, Lavoisier and Laplace were already measuring heat quantities from the animal respiration process (Kleiber, 1961).⁽²⁾ Bomb-combustion calorimetry, which was developed at the end of the nineteenth century, was applied on animal and plant materials, including food and metabolic products. Results from these measurements and from continued calorimetric studies of heat production from animals, including humans, were of great importance for the development of modern biological energetics. At the present time, biocalorimetric work is conducted at levels of different complexity (see table 1, cf. Wadsö⁽³⁾).

TABLE 1.

1. Water, simple model compounds
2. Low molecular biochemical compounds
3. Biopolymers, lipid aggregates
4. Cell organelles
5. Living cells
6. Animals, plants
7. Eco-systems

For comprehensive reviews, see Spink and Wadsö,⁽⁴⁾ Marini and Martin,⁽⁵⁾ Wadsö⁽³⁾ and various chapters in the monographs edited by Jones⁽⁶⁾ and Beezer.⁽⁷⁾

Water is a key compound in biological processes. It is the general solvent for polar substances and ions and it participates in biochemical reactions. Its inability to dissolve many nonpolar substances is also of great importance. Molecules of dual nature, amphiphiles, are forced to adopt unique orientations in water, forming suitably organized structures. Such molecules play a prominent role in the formation of, for instance, the lipid bilayer in cell membranes. Thermodynamic properties of solutions of simple organic compounds, where water is involved as solute or solvent, contribute, not only to our knowledge of physical chemistry in general, but also to our understanding of biochemical or biological processes.

This work deals partly with the development and testing of new microcalorimetric vessels for dissolution of easily and/or slightly soluble liquids (I) and slightly soluble solids (II) in water. By use of the vessel described in paper I, dissolution measurements were performed on simple model compounds such as alcohols (III) and esters (IV). Microcalorimetric measurements of the transfer of water into hydrocarbons (V) and into alcohols and esters (VI) have also been performed.

2. SOME CALORIMETRIC PRINCIPLES

For an introduction to calorimetry, see e.g. Sturtevant (1971),⁽⁸⁾ Spink and Wadsö (1976),⁽⁴⁾ Marini and Martin (1979),⁽⁵⁾ Spink (1980)⁽⁹⁾ and Wadsö (1986)⁽¹⁰⁾.

Depending on the processes to be measured, calorimetric vessels are designed as batch or flow-through vessels and are often equipped with a stirrer and a titration unit. The common term "microcalorimeter" usually refers to a very sensitive calorimeter in which small sample quantities (micro moles) react. Most microcalorimeters are designed as twin, or differential instruments, where one vessel usually contains inactive material of the same heat capacity as the reaction system in the other vessel. Disturbances are expected to influence the two vessels in the same way, causing the differential signals to cancel each other; the contribution to the differential signal is thus zero.

In the present work, adiabatic, isoperibolic and thermopile heat-conduction calorimeters have been used.

2a. Adiabatic calorimeters

There is no net heat exchange between the calorimetric vessel and the surroundings in an adiabatic calorimeter. The observed temperature change ΔT is thus directly proportional to the heat quantity q absorbed or evolved in the vessel:

$$q = \epsilon \Delta T. \quad (1)$$

Ideally, the calibration constant ϵ is identical to the heat capacity of the vessel and its content.

$$dq/dt = k(T_S - T_V) \quad (2)$$

Equation (2) shows Newton's law of cooling, where dq/dt is the heat flow per unit of time, k is the thermal conductivity and T_V and T_S are the temperatures of the calorimetric vessel and its

surroundings, respectively. No net heat exchange is obtained when $k = 0$ or $T_s = T_v$. It is very difficult to reach adiabatic conditions by thermal insulation ($k = 0$) of the vessel, and these conditions are therefore usually approached by other means. For exothermic processes, T_v will increase. A common method for maintaining $T_s = T_v$ is to insert an "adiabatic shield" between the vessel and the thermostated bath (see figure 1). By heating the shield electrically, $T_s = T_v$ can be satisfied during the experiment. For endothermic processes T_v will decrease; this can be compensated for by electrical heating of the calorimetric vessel. This principle is used in the enthalpy of vaporization measurements in the present work (IV). Adiabatic calorimeters are of great importance for studies of slow reactions, in which a time span of hours may be required for an experiment.

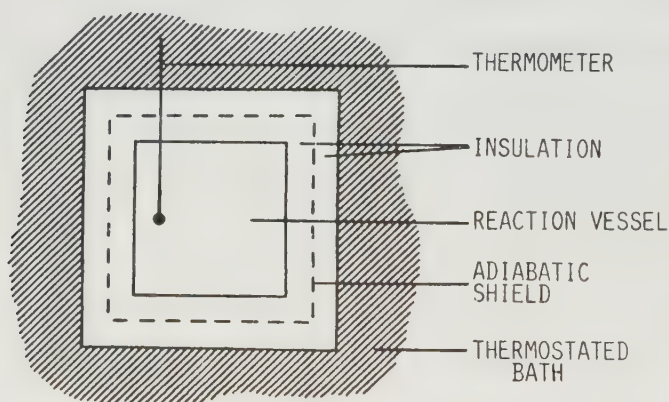


Figure 1. Principle design of an adiabatic calorimeter.

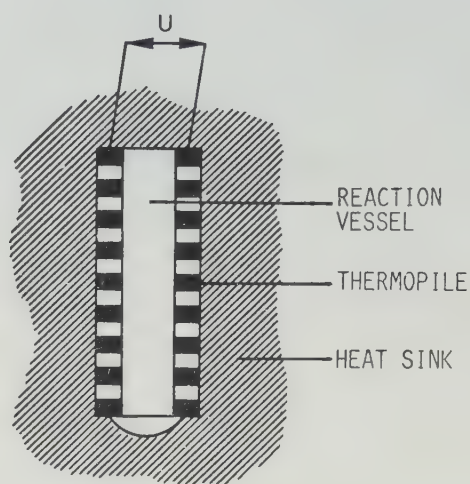
2b. Isoperibolic calorimeters

In an isoperibolic calorimeter the temperature of the environment of the calorimetric vessel is kept constant. During an experiment, T_v will change and $T_v \neq T_s$, leading to an exchange of heat with the surroundings, equation (2). The ΔT measured will thus include a contribution from the heat exchange, which can be corrected for

through evaluations made by the methods of Regnault-Pfaundler or Dickinson described in reference 11. The correction term will increase with the time required for an experiment and isoperibolic calorimeters are thus particularly useful for fast reactions. An isoperibolic "macro"-calorimeter (LKB 8721-1) has been used in the measurements of dissolution of the lower alcohols in H_2O (III).

2c. Thermopile heat-conduction calorimeters

Figure 2. Schematic picture of a section through a thermopile heat conduction calorimeter.



When the temperature of the calorimetric vessel is different from that of the surrounding heat sink, heat flows through the thermopile wall and the temperature difference gives rise to a proportional voltage signal U (see figure 2). Tian's equation (3) gives the thermal power P developed in the vessel as a function of U :

$$P = \epsilon[U + \tau(dU/dt)], \quad (3)$$

where ϵ is the calibration constant, dU/dt is the time derivative of the voltage signal and τ is the time constant defined by $\tau = C/k$, where C and k are "practical" values for the heat capacity of the

vessel and its content, and the thermal conductivity through the thermopile wall, respectively.

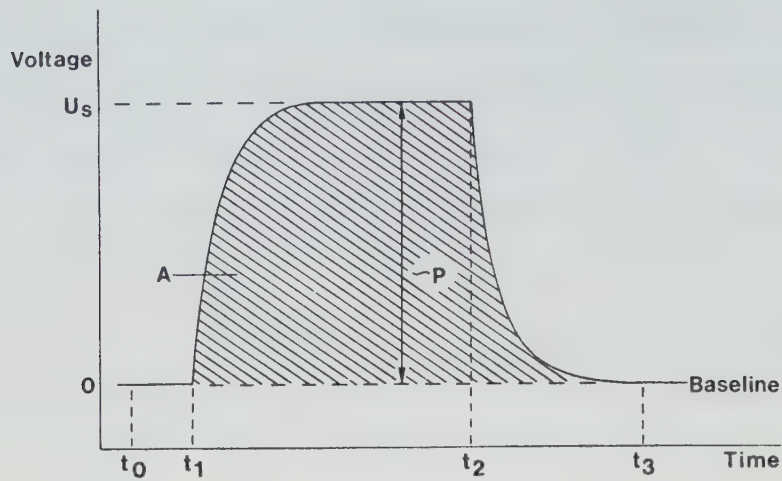


Figure 3. Voltage-time curve from a thermopile heat-conduction calorimeter. A constant heat production was released between t_1 and t_2 . The baseline displacement during the steady state conditions U_s is directly proportional to the thermal power P . The voltage-time integral between t_0 and t_3 , represented by the shaded area A , is proportional to the total heat released.

Figure 3 shows a typical voltage-time curve for constant power between t_1 and t_2 . For steady-state conditions, $dU/dt = 0$ and equation (3) reduces to

$$P = \epsilon U, \quad (4)$$

and the instrument can be used as a watt-meter. Integration of equation (3) between t_0 and t_3 gives the total heat released q :

$$q = \epsilon \int_{t_0}^{t_3} U dt + \epsilon \tau [U(t_3) - U(t_0)].$$

Normally $U(t_0) = U(t_3)$ and equation (5) reduces to

$$q = \epsilon \int_{t_0}^{t_3} U dt, \quad (6)$$

where $\int_{t_0}^{t_3} U dt$ corresponds to the shaded area A in figure 3.

The heat-conduction principle is very common for microcalorimeters and instruments based on this principle have been used for most of the measurements described in this thesis.

3. SOLUTION CALORIMETRY

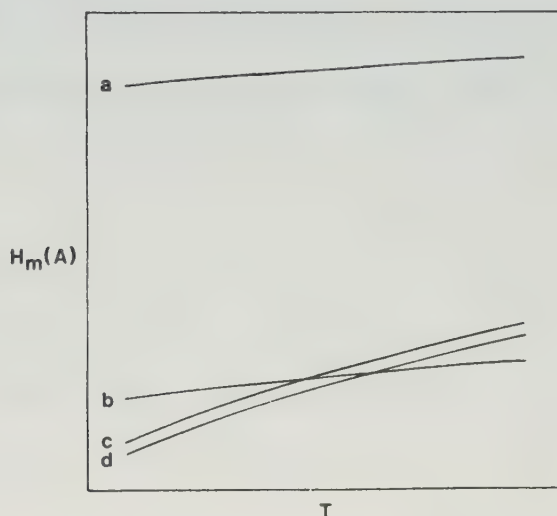


Figure 4. Schematic picture of the enthalpy content, $H_m(A)$, for one mole of A as a function of the temperature T .
a, $A(g, p = 1 \text{ atm, ideal})$; b, $A(l \text{ or } s)$; c, $A(aq, n \cdot H_2O)$, and d, $A(aq, \infty \cdot H_2O)$.

Process	Molar enthalpy change
$b \rightarrow a$ or $A(l) \rightarrow A(g, p = 1 \text{ atm, ideal})$	$\Delta_{\text{vap}} H_m^0$
$b \rightarrow c$ or $A(l) + n \cdot H_2O(l) \rightarrow A(aq, n \cdot H_2O)$	$\Delta_{\text{solv}} H_m$
$b \rightarrow d$ or $A(l) + \infty \cdot H_2O(l) \rightarrow A(aq, \infty \cdot H_2O)$	$\Delta_{\text{solv}} H_m^\infty$
$c \rightarrow d$ or $A(aq, n \cdot H_2O) + \infty \cdot H_2O(l) \rightarrow A(aq, \infty \cdot H_2O)$	$\Delta_{\text{dil}} H_m^\infty$
$a \rightarrow c$ or $A(g, p=1 \text{ atm, ideal}) + n \cdot H_2O(l) \rightarrow A(aq, n \cdot H_2O)$	$\Delta_{\text{solv}} H_m$
$a \rightarrow d$ or $A(g, p=1 \text{ atm, ideal}) + \infty \cdot H_2O(l) \rightarrow A(aq, \infty \cdot H_2O)$	$\Delta_{\text{solv}} H_m^\infty$

Figure 4 illustrates the enthalpy contents of the compound A in different states as a function of the temperature. No values can be assigned the enthalpy content unless a value for a reference state has been defined. However, values for differences in molar enthalpy content, $\Delta H_m(A)$, between two states can always be derived. The symbol Δ does not tell us anything about the two states; therefore further symbols have to be added so as to define the process. At each temperature, the states a, b and d are well-defined, whereas the amount of water has to be known in the state c. The symbols used are shown immediately after figure 4.

If the state c is identical in all processes, the following equations are derived at each temperature according to Hess's law:

$$\Delta_{\text{sol}} H_m^\infty = \Delta_{\text{sol}} H_m + \Delta_{\text{dil}} H_m^\infty \quad (7)$$

$$\Delta_{\text{sol v}} H_m^\infty = \Delta_{\text{sol}} H_m^\infty - \Delta_{\text{vap}} H_m^0 \quad (8)$$

The molar heat capacity $C_{p,m}(A)$ is defined by

$$C_{p,m}(A) = dH_m(A)/dT, \quad (9)$$

and is represented by the slopes of the curves a to d (figure 4) at each temperature. Taking the process $b \rightarrow d$ and the variation in $\Delta_{\text{sol}} H_m^\infty$ with the temperature as an example, one can derive a $\Delta_{\text{sol}} C_{p,m}^\infty$. This value represents the difference between the slopes of the curves b and d at a certain temperature. The $\Delta_{\text{sol}} C_{p,m}^\infty$ is thus identical to

$$C_{p,m}[A(\text{aq}, \infty \cdot \text{H}_2\text{O})] - C_{p,m}[A(l)]$$

or

$$C_{p,m,2}^\infty - C_{p,m}^*$$

The partial molar heat capacity for A in infinitely dilute aqueous solution, $C_{p,m,2}^{\infty}$ or $C_{p,2}^{\infty}$, is obtained by

$$C_{p,2}^{\infty} = \Delta_{\text{sol}} C_{p,m}^{\infty} + C_{p,m}^{\star}, \quad (10)$$

where $C_{p,m}^{\star}$ is the heat capacity for the pure compound A.

In "macro" solution calorimetry the dissolution process is normally initiated by breaking an ampoule containing the liquid or solid solute into a certain amount of solvent. For instance, the LKB-8721 instrument is normally used with an ampoule of 1 cm^3 and a vessel of 25 or 100 cm^3 . This instrument is very useful for measurements with easily soluble liquid or solid compounds, for which the enthalpy values can be determined with an accuracy of about 0.2 per cent.

However, accurate measurements of compounds with low solubility in water, as for instance n-pentan-1-ol, are difficult to make with that instrument. The dissolution process is facilitated by using flow-microcalorimeters, where the amount of solvent can be increased.

3a. Dissolution of slightly soluble gases

Designs of flow-microcalorimeters for dissolution of slightly soluble gases in water were reported by Gill and Wadsö in 1982⁽¹²⁾ and by Dec and Gill in 1984.⁽¹³⁾ These instruments have been used to determine the enthalpy of solution in water of rare gases and some hydrocarbons.^(14,15) The design of these instruments is related to the design of the calorimeter for dissolution of slightly soluble liquids, see below (3b).

3b. Dissolution of slightly soluble liquids (paper I).

A flow-microcalorimeter for dissolution of slightly soluble liquids in water was reported by Gill and Wadsö in 1975.⁽¹⁶⁾ The solute was introduced into a stream of water in a Teflon tube. The hydrophobic liquid, which will adhere to the Teflon, then forms a thin film on the Teflon surface; this will facilitate the dissolution process. This design has been used in dissolution measurements of different groups of liquid compounds such as benzene derivatives⁽¹⁷⁾ and alkanes.⁽¹⁸⁾

However, in measurements of some slightly soluble esters, samples were shown to adhere poorly to the Teflon surface and to have a tendency to pass through the dissolution zone without being dissolved. Furthermore, volatile compounds such as benzene and methyletanoate could leak from the barrel of the syringe through the Teflon seal of the plunger. In addition, comparisons between related flow-microcalorimetric vessels showed that the position of the electrical calibration heater is very critical and can cause systematic errors. These factors caused us to undertake a further development and testing of the calorimetric vessel, which is reported in paper (I).

During the course of the work, several new design principles and materials were investigated. The original Teflon material was shown to be the most efficient one, but in the final design, used in the present work, the dissolution tube system was extended by an outer flow line in the space between the Teflon tube and an outer steel tube (see figure (1,I)). When the Teflon tube and the outer steel tube are formed into a spiral, contact points between the two materials are created. These contact points may possibly be responsible for keeping small droplets of the solute in the vessel. For compounds which form a poor film on the Teflon surface, the time period required for

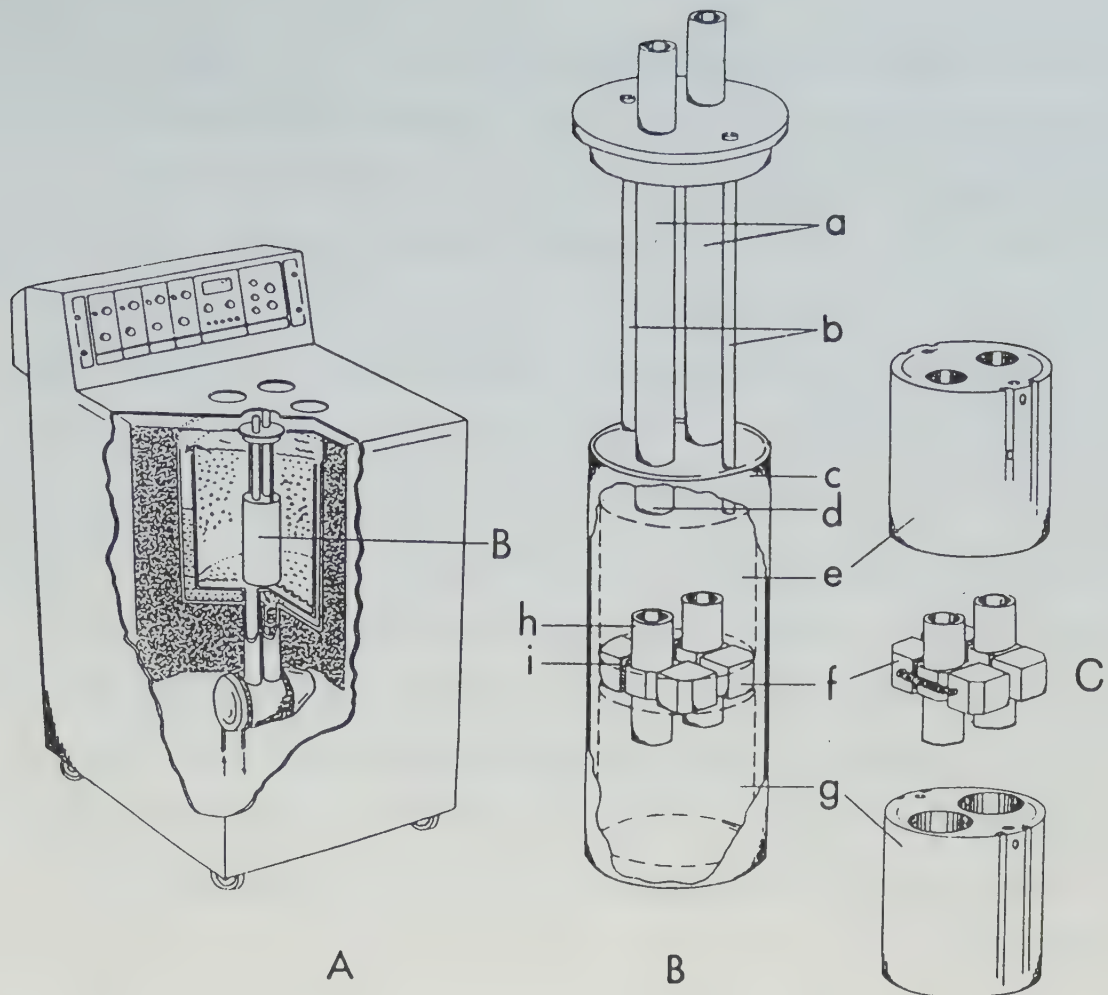


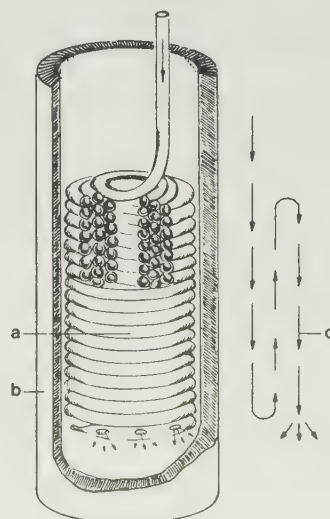
Figure 5. Four-channel microcalorimeter (prototype for LKB's "BioActivity Monitor").

A. Cutaway view of the instrument shown with one channel B positioned in the water bath. C is the twin calorimeter unit.

a, b, thin-walled steel tubes; c, steel cylinder; d, plastic (Ryton) tube; e, g, aluminium bolts serving as main heat sinks; f, aluminium block; h, aluminium tube (holder for insertion vessel); i, thermocouple plate.

(Suurkuusk and Wadsö 1982). (19)

Figure 6. Vessel for dissolution of liquids. The coiled Teflon tube a is positioned in the sample compartment b (compare 1 in figure (1B,V)). c shows the flow mode schematically.



dissolution will increase. This necessitates a very stable temperature in the surrounding water-bath. For the measurements on n-octan-1-ol and glycerol-tributanoate (reported in papers (III) and (IV), respectively), a spiral-shaped Teflon tube was used in a calorimetric vessel which fits the commercial version (2277 multichannel micro-calorimeter system, LKB Produkter, Bromma, Sweden) of the calorimeter (see figure 5).^(19, 20) The temperature stability of the water bath used with this calorimeter is $\pm 1 \times 10^{-4}$ K for periods longer than a day. Figure 6 shows a picture of the Teflon spiral positioned in the sample compartment. For most of the experiments a metal core was inserted into the coils of the Teflon spiral so as to force the solvent to flow in the space between the spiral and the sample compartment. Further work is now being conducted on this principle in our laboratory and new materials are being tested. That work will be reported elsewhere.⁽²¹⁾

The problem of leakage of volatile compounds through the Teflon tip of the syringe plunger was shown to be minimized by a mercury seal between the plunger and the barrel of the syringe (see figure (3,I)). The diffusion at the tip of the hypodermic needle was significant for easily soluble compounds in water, such as the lower alcohols. Table (2,I) shows that the rate of diffusion and/or leakage is greater for vessel 2 than for vessel 1. In these measurements, two syringes with different injection needles were used, i.d. = 0.15 mm (vessel 1) and i.d. = 0.22 mm (vessel 2). The diffusion effect can be reduced by minimizing the inner diameter of the needle, but this leads frequently to clogging effects. By running the experiments with identical injection rates but using different injection periods and keeping the time between the injections constant, one will arrive at identical diffusions and leakage states at the beginning of each injection. (The first injection should be excluded.) Results from experiments

performed in this way can be evaluated by use of equation (6,I), which makes corrections for the diffusion and leakage. The calorimetric vessel is thus useful not only for slightly soluble liquids, but also for easily soluble liquids in water.

The electrical calibrations performed with the heaters o and p, figure (1,I), led to different calibration constants ϵ (see table (1,I)), with the highest value of ϵ for the outer heater o. This is probably because the solvent is heated close to the flow outlet and will transport a disproportional amount of heat out of the vessel. The inner heater p is positioned closer to the dissolution zone and the corresponding ϵ gives a more accurate enthalpy value for the substance. However, we have found that the most accurate ϵ is obtained by use of a chemical process, for instance the dissolution of propan-1-ol in water to infinite dilution. As can be seen in table (2,I), enthalpy values based on this chemical calibration are in excellent agreement with results obtained by use of "macro" solution calorimeters. The dissolution zone for the least soluble compounds measured can differ from that of propan-1-ol, but will hardly pass the T-junction k (figure (1,(I))). Therefore, we believe that the possible systematic errors in these enthalpy values are less than 0.5 per cent.

3c. Dissolution of slightly soluble solids (paper II)

A design of a flow-calorimetric vessel for dissolution of slightly soluble solids in water was reported by Gill and Seibold in 1976.⁽²²⁾ In their instrument the solid sample was protected from premature contact with the solvent by an air space. In paper (II), another flow vessel for dissolution of slightly soluble solids is described. This vessel, which is based on a perfusion and titration

vessel recently developed in our laboratory,⁽¹⁹⁾ is used with the LKB 2277 multichannel microcalorimeter system⁽²⁰⁾ (LKB Produkter, Bromma, Sweden).

The vessel was tested by dissolution of acetanilide and adenine in water at different temperatures. The results reported for adenine are in full agreement with results of a very careful study by Kilday,⁽²³⁾ using a "macro" solution calorimeter where about 200 mg of the sample are dissolved in 300 cm³ of water.

4. THE HYDROPHOBIC EFFECT

Hydrophobic substances are typically soluble in nonpolar solvents, but sparingly soluble in water. Nonpolar compounds such as alkanes and rare gases are examples of such substances.

The solvation processes of these compounds in water, "hydrophobic hydration", is characterized at room temperature by a favourable negative enthalpy change^(18, 24) and an unfavourable negative entropy change.^(24, 25) These thermodynamic properties were first pointed out in a classic paper by Evans and Franks in 1945;⁽²⁴⁾ they are not restricted to nonpolar compounds only, but also appear in the solvation process of molecules carrying apolar groups, such as those of alcohols, amines, esters, etc. Evans and Franks concluded that hydrophobic hydration led to a more rigid (ice-like) structure of water around the hydrophobic part of the solute.

The entropy effect associated with hydrophobic hydration has important consequences for mutual interactions between hydrophobic groups dissolved in water. In order to reduce the low-entropy region of hydrophobic hydration, hydrophobic molecules or groups tend to aggregate. This phenomenon, which can be looked upon as a reversal of

the dissolution process, is called the "hydrophobic interaction". The term "hydrophobic bonding", which is sometimes used, is misleading, as it gives an appearance of strong attractive forces between the hydrophobic species. From measurements of the surface tension of the pure liquids and the interfacial tension at a hydrocarbon-water interface at 298 K, Tanford⁽²⁶⁾ found that the attraction of hydrocarbon to itself is essentially the same as its attraction to water. It is thus more likely that the strong attraction between water molecules is responsible for the hydrophobic interaction. This property has been found to be very important in structure-forming processes in water.⁽²⁵⁾ For instance, the folding of the peptide chain in such a way that the hydrophobic parts are concentrated to the interior of the protein, the formation of lipid bilayers of biological membranes, and the formation of micelles are all examples of this effect.

The enthalpy change of the dissolution of hydrophobic compounds in water at room temperature is small and normally within a few $\text{kJ} \cdot \text{mol}^{-1}$. The temperature dependence of the enthalpy change $\Delta_{\text{sol}} C_{\text{p,m}}^{\infty}$ is large and positive, which leads to abnormally large partial molar heat capacities at infinite dilution $C_{\text{p,2}}^{\infty}$. For simple (non-ionic) hydrophobic compounds, $C_{\text{p,2}}^{\infty}$ -values can normally be precisely predicted from simple additivity schemes.⁽²⁷⁻²⁹⁾ The high additivity has led to the conclusion that the hydrophobic hydration effect reflected by the large heat capacity is a short-range effect.⁽²⁷⁾ It has been suggested that the excess heat capacity is connected with temperature-dependent structural properties of the first solvation shell around the hydrophobic group.^(27, 30, 31)

4a. Dissolution of n-alkan-1-ols in H₂O (paper III)

In this paper, calorimetric measurements of dissolution of n-alkan-1-ols in H₂O (C₁ to C₈) are reported. For the measurements of C₁- to C₄-alcohols in H₂O, two different calorimeters were used; an LKB-8721-1 precision solution calorimeter and the flow-microsolution calorimeter reported in paper (I). It was shown that results obtained with the former calorimeter were more precise, but these measurements are more time-consuming than measurements with the latter calorimeter, which is automatically controlled. The LKB calorimeter cannot be used for accurate measurements of the C₅- to C₈-alcohols.

Figure (4,III) shows the enthalpies of solvation $\Delta_{\text{solv}} H_m^\infty$ plotted against the number N_c of carbon atoms. The initial state is that of the molecules in the ideal-gas state and the enthalpy change corresponding to the process is thus due to the solute-solvent interaction. It is interesting to note the long-range influence (three to four carbon atoms) of the hydroxyl group on the solvent medium.

The partial molar heat capacities $C_{p,2}^\infty$ at 298.15 K are plotted against N_c in figure (5,III). It is seen that our simple additivity scheme⁽²⁷⁾ works properly. As observed earlier,⁽²⁷⁾ the intercept value $76 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, which corresponds to $C_{p,2}^\infty$ for water dissolved in water, is in excellent agreement with the heat capacity for pure water, $75 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. This may be fortuitous, but the high additivity (even at $N_c = 0$) indicates a short-range effect, where the hydrogen atoms seem to play an important role.

Dilution experiments in H₂O showed pairwise interaction coefficients h_{xx} increasing with the alkyl chain length. For low values of the molality m , $\Delta_{\text{dil}} H_m$ can be obtained by

$$\Delta_{\text{dil}} H_m^\infty = - h_{xx} m \quad (11)$$

The mean final solute molality is estimated to decrease with increasing alkyl chain length in the flow-microcalorimetric measurements. For instance, m is estimated to be less than $6 \times 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$ for the dissolution experiments with *n*-octan-1-ol. Assuming $h_{xx} < 20 \text{ kJ} \cdot \text{kg} \cdot \text{mol}^{-2}$, the correction $|\Delta_{\text{dil}} H_m^\infty| < 0.012 \text{ kJ} \cdot \text{mol}^{-1}$, which is negligible in comparison with the uncertainties in the $\Delta_{\text{sol}} H_m^\infty$ values.

4b. Dissolution of some esters in H_2O . (paper IV)

Calorimetric dissolution measurements of some esters in H_2O were performed at different temperatures. By use of $\Delta_{\text{vap}} H_m^0$ values, $\Delta_{\text{sol}} H_m^\infty$ were derived according to equation (8) at 298.15 K.

Figure (1,IV) shows a small but significant difference of about $1.7 \text{ kJ} \cdot \text{mol}^{-1}$ between the enthalpy values of the methylesters and ethylesters with an identical number of alkyl carbon atoms. That difference seems to be due to a greater influence from the ester group on the solvation of CH_2 or CH_3 attached to the ether oxygen in the ester group. It should be noted that the influence on the solvation enthalpy of the CH_2 groups adjacent to the functional group is more pronounced for the hydroxyl group than for the ester group (see figures (4, III) and (1, IV)). Della Gatta et al.⁽³²⁾ have earlier found that branching of the alkyl chain for methylesters leads to less negative $\Delta_{\text{sol}} H_m^\infty$ values than in unbranched chains. That observation agrees with the present result for ethyl-2,2-dimethylpropanoate, which can also be seen in figure (1,IV). The monoesters (except ethyl-2,2-dimethylpropanoate) and the diesters are all straight-chain compounds. Group contributions for $\Delta_{\text{sol}} H_m^\infty$ at 298.15 K were derived for these compounds. Table (3,IV) shows the experimental and the calculated

$\Delta_{\text{soln}} H_m^\infty$ values based on these group parameters.

As was discussed in sections 4 and 4a, the $C_{p,2}^\infty$ values are of great interest in connection with the hydrophobic effect, and the remarkable role seemingly played by the hydrogen atoms was pointed out. The group contribution to $C_{p,2}^\infty$ from the ester group (which does not include any hydrogens) is $-7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ as derived from the monoesters. This value is not significantly different from zero when the uncertainty is taken into account. In figure (2, IV), the contributions to $C_{p,2}^\infty$ from the hydrophobic part of the molecule (excluding contributions from the ester groups) are plotted against the number of hydrogen atoms. The figure would not have changed significantly if the contributions from the ester groups had been included. It is seen that the point for glyceroltributanoate falls significantly below the line, with a deviation corresponding to the contribution from one CH_2 group. The deviation can be explained with intramolecular hydrophobic interactions between the rather long alkyl chains, which will partially shield each other from water contact.

5. WATER AS SOLUTE

Two papers concern the investigation of the enthalpy of solution of water into liquid phases. Very few accurate data of this kind are available for compounds in which the water solubility is limited.

5a. Dissolution of H_2O in hydrocarbons (paper V).

A calorimetric technique in which water is titrated into the liquid n-alkanes is not possible because of the low water solubility of the n-alkanes (less than 100 p.p.m. by mass at 298.15 K for C_7 and higher homologous).⁽³³⁾ In these measurements small amounts of the liquid hydrocarbons with different water content were injected into an equilibrated two-phase system of the hydrocarbon and water, saturated

with each other. Thus the process measured was the water saturation of the amount of injected hydrocarbon.

Determinations of the water content of a hydrocarbon sample varied with different syringe fillings. It was therefore necessary to perform these measurements from the same syringe filling as was used in the calorimetric measurements. Calibrations with a sample of well-known water content must then be made so as to know the water content in the hydrocarbon. For reasons described above, accurate calibration measurements of samples of low water content are difficult to perform. The problem was avoided by plotting the enthalpy values against the corresponding integrals A from the g.c. measurements (see figures (2, V) and (3, V)). Extrapolating to $A = 0$ corresponds to the enthalpy change when the dry sample is saturated with water. Using literature values for the water solubility, the molar enthalpies of solution $\Delta_{\text{sol}}H_m$ were derived. The water solubilities were measured by use of the Karl Fisher method on larger volumes of saturated hydrocarbons.⁽³³⁾ The linear relations shown in figures (2, V) and (3, V) indicate that the partial molar enthalpies are identical in the whole concentration range and can be taken to be equal to $\Delta_{\text{sol}}H_m^\infty$.

At 298.15 K there is no significant difference in the $\Delta_{\text{sol}}H$ values for dissolution in the n-alkanes (mean value = $(34.9 \pm 1.6) \text{ kJ} \cdot \text{mol}^{-1}$ [†]); the value for benzene is $(24.4 \pm 0.5) \text{ kJ} \cdot \text{mol}^{-1}$, indicating a stronger interaction between H_2O and benzene. The $\Delta_{\text{sol}}C_{p,m}$, which was found to be close to zero, and the constant $\Delta_{\text{sol}}H_m$ for different n-alkanes led to equation (5, V), which describes the water solubility of the n-alkanes as a function of temperature and the number of carbon atoms.

[†] The uncertainty given is twice the standard deviation of the mean.

5b. Dissolution of H_2O in alcohols and esters (paper VI).

The higher solubility of water in the alcohols and esters in comparison with the hydrocarbons permitted a calorimetric technique in which small amounts of water were consecutively titrated into the solvent. The integral enthalpy changes were considered as the partial molar enthalpies of solution $\Delta_{sol}H_m(X_w)$ corresponding to the molar fraction X_w of water, when half the amount of water at each step was injected. By extrapolating to $X_w = 0$, $\Delta_{sol}H_m^\infty$ was obtained.

Figure (4, VI) shows a plot of $\Delta_{sol}H_m^\infty$ against the number N_C of carbon atoms at 298.15 K. It is seen that the interactions between H_2O and methanol or ethanol are stronger than those between the H_2O molecules themselves, and an essentially constant enthalpy change of about 3.3 kJ mol^{-1} is obtained for the n-alkan-1-ols C_7 to C_{10} .

A weak increase in $\Delta_{sol}H_m^\infty$ with increasing alkyl chain length is seen for the methylester. Methylbutanoate, ethyleneglycoldibutanoate and glyceroltributanoate all have the same ratio N_C/N_F , where N_F is the number of functional groups. It is interesting to note that the esters also have identical $\Delta_{sol}H_m^\infty$ values, which can be seen in figure (5, VI).

However, recent measurements in our laboratory on glycerol, which has the same ratio N_C/N_F as methanol, showed $\Delta_{sol}H_m^\infty = -(1.38 \pm 0.02) \text{ kJ}\cdot\text{mol}^{-1}$, whereas for methanol $\Delta_{sol}H_m^\infty = -(2.99 \pm 0.04) \text{ kJ}\cdot\text{mol}^{-1}$. Further measurements are needed to investigate the difference in this property between alcohols and esters.

6. OUTLOOK

With the new flow-microcalorimetric instrumentation documented here, extended studies of interesting simple model compounds are possible, for instance:

- n-nonan-1-ol and n-decan-1-ol (at least at higher temperatures), to complete data for a very long homologous series.
- slightly soluble polyols (easily soluble polyols have been shown⁽³⁴⁾ to deviate from our simple additivity scheme⁽²⁷⁾ for $C_{p,2}^{\infty}$).
- halogenated hydrocarbons.
- peptides.

The technique used for the 'dissolution of water into hydrocarbons (paper V) can also be applied to other compounds so as to obtain the integral enthalpy change for dissolution of water to saturation, an area where there are very few data so far.

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REFERENCES

1. Armstrong, G. T. J. Chem. Educ. 1964, 41, 297.
2. Kleiber, M. The Fire of Life. Wiley: New York, 1961.
3. Wadsö, I. Pure and Appl. Chem. 1983, 55, 515.
4. Spink, C. H.; Wadsö, I. Methods of Biochemical Analysis, Vol. 23, pp. 1-158. Glick, D.; editor. Wiley-Interscience: New York, 1976.
5. Marini, M. A.; Martin, C. J. CRC Crit. Rev. Anal. Chem. 1979, 8:3, 221-283.
6. Biochemical Thermodynamics. Jones, M. N.; editor. Elsevier: Amsterdam, 1979.
7. Biological Microcalorimetry. Beezer, A. E.; editor. Academic Press: London, 1980.
8. Sturtevant, J. M. Physical Methods of Chemistry, Vol. 1, Part V, pp. 347-425. Editors: Weissberger, A. and Rossiter, B. W. Wiley: New York, 1971.
9. Spink, C. H. CRC Crit. Rev. Anal. Chem. 1980, 9:1, 1-95.
10. Wadsö, I. In Thermal and Energetic Studies of Cellular Biological Systems. James, A. M.: editor. Adam Hilger Ltd.: Bristol. 1986.
11. Wadsö, I. Science Tools, 1966, 13, 33.
12. Gill, S. J.; Wadsö, I. J. Chem. Thermodyn. 1982, 14, 905.
13. Dec, S. F.; Gill, S. J. Rev. Sci. Instr. 1984, 55, 765.
14. Olofsson, G.; Oshodi, A. A.; Qvarnström, E.; Wadsö, I. J. Chem. Thermodyn. 1984, 16, 1041.
15. Dec, S. F.; Gill, S. J. J. Solution Chem. 1984, 13, 27.
16. Gill, S. J.; Wadsö, I. J. Chem. Thermodyn. 1975, 7, 175.
17. Nichols, N.; Wadsö, I. J. Chem. Thermodyn. 1975, 7, 329.
18. Gill, S. J.; Nichols, N. F.; Wadsö, I. J. Chem. Thermodyn. 1976, 8, 445.

19. Görman Nordmark, M.; Laynez, J.; Schön, A.; Suurkuusk, J.; Wadsö, I. J. Biochem. Biophys. Methods 1984, 10, 187.
20. Suurkuusk, J.; Wadsö, I. Chemica Scripta 1982, 20, 155.
21. Hallén, D.; Nilsson, S.-O.; Wadsö, I. To be published.
22. Gill, S. J.; Seibold, M. L. Rev. Sci. Instrum. 1976, 47, 1399.
23. Kilday, M. V. J. Res. Nat. Bur. Stand. 1978, 83, 347.
24. Evans, M. W.; Frank, H. S. Chem. Phys. 1945, 13, 507.
25. Tanford, C. The Hydrophobic Effect: Formation of Micelles and Biological Membranes. 2nd Edition. Wiley-Interscience: New York, 1980.
26. Tanford, C. Proc. Nat. Acad. Sci. 1979, 76, 4175.
27. Nichols, N.; Sköld, R.; Spink, C.; Suurkuusk, J.; Wadsö, I. J. Chem. Thermodyn. 1976, 8, 1081.
28. Guthrie, J. P. Can. J. Chem. 1977, 55, 3700.
29. Cabani, S.; Gianni, P.; Leporia, L.; Mollica, V. J. Solution Chem. 1981, 10, 563.
30. Gill, S. J.; Wadsö, I. Proc. Natl. Acad. Sci. 1976, 73, 2955.
31. Dec, S. F.; Gill, S. J.; Olofsson, G.; Wadsö, I. J. Phys. Chem. 1985, 89, 3758.
32. Della Gatta, G.; Stradella, L.; Venturello, P. J. Solution Chem. 1981, 10, 203.
33. Schatzberg, P. J. Phys. Chem. 1963, 67, 776.
34. Lian, X.-N.; Chen, A.-T.; Suurkuusk, J.; Wadsö, I. Acta Chem. Scand. 1982, A36, 735.

I

A flow-microcalorimetric vessel for solution of small quantities of easily or slightly soluble liquids. Solution of benzene in water at 298.15 K

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A flow-calorimetric vessel has been designed for the determination of enthalpies of solution of very small quantities of liquids. The design has been chosen with particular reference to water as solvent but can be used for any non-viscous liquid. The instrument can be used for measurements of slightly soluble compounds as well as for easily soluble compounds. During the measurements, mm^3 quantities of solute are injected into a stream of solvent by use of a modified Hamilton syringe. Final concentrations of the solutes are in the range of (1 to 6) $\text{mol} \cdot \text{m}^{-3}$. Measurements are performed by a fully automatic procedure. Electrical and chemical calibration methods have been compared and a method for correction of small leakage and diffusion effects is presented. The instrument has been tested by solution of methanol, ethanol, propan-1-ol, butan-1-ol, and benzene in water at 298.15 K.

1. Introduction

A few years ago we reported a flow-microcalorimetric technique for determination of molar enthalpies of aqueous solution of slightly soluble (hydrophobic) liquids.⁽¹⁾ With that method a small quantity of solute (a few mm^3) is injected into a slow stream of water flowing through a Teflon tube, made in the form of a spiral and forming the calorimetric vessel. The hydrophobic liquid, which will adhere to the Teflon, then forms a thin film inside the Teflon spiral. The solute will thus form a large contact area with the solvent and efficient dissolution can take place. The method was successfully applied to several hydrocarbons in the temperature range 288 to 308 K, leading to values for $\Delta_{\text{sol}} H_{\text{m}}$ as well as $\Delta_{\text{sol}} C_{p, \text{m}}$.^(1, 2)

However, subsequent work with the instrument suggested that the method should be further developed so as to rule out some possibilities of significant systematic errors. It was shown by C. Criss (on leave from University of Miami, Coral Gables, Florida, U.S.A.) that during the equilibration period a small amount of hydrophobic solute (benzene) could pass through the wall of a Teflon tube attached to the end of the injection needle. This effect could possibly cause a significant systematic error for some substances. Experiments with some disulphides and halogenated hydrocarbons indicated that significant amounts of these compounds were

irreversibly trapped in the relatively large mass of Teflon used in the dissolution vessel. A different effect was observed with some slightly soluble esters which were shown to adhere poorly to the Teflon tube and to have a tendency to pass through the dissolution zone of the flow cell without being dissolved. Further, results of systematic studies of electrical calibrations of related flow-calorimetric vessels⁽³⁾ suggested that the position and the design of the electrical calibration heater are more critical than we had realized earlier.

Extensive experimental work was carried out and several new design principles and materials were tested. It was concluded that the original dissolution method remained the most efficient for solution of soluble compounds in water. However, the work led gradually to significant changes in the mechanical design of the instrument and in working procedures. The new instrument has also shown itself to be useful for precise measurements of easily soluble compounds.

The injection technique has been modified, syringe leakage problems have been analyzed, and the measure measurement procedure has been made fully automatic.

2. Experimental

APPARATUS

A glass vessel, forming a counter-current heat-exchange system, was attached to a metal dissolution vessel, figure 1. The outer design of the vessel is similar to our recently reported gas-solution vessels⁽³⁾ and is used with the same type of twin heat-conduction calorimeter.⁽⁴⁾ The vessel is constructed of two concentric glass tubes (b, c). To increase the heat exchange between them, the inner tube consists of a series of bulbs joined by short lengths of tubing. The vessel has three thermally conducting metal regions (d, e, f). The lowest, f, consists of a brass cup which contains the dissolution region of the flow system and fits into the sample holder of the calorimeter. The other conducting regions (d, e) provide thermal shorting to the calorimeter heat sink and the thermostatic bath, respectively. These regions consist of brass tubes (o.d. 25 mm) and the annular space between them and the outer glass tube c is filled with Wood's metal.⁽³⁾

Figure 1(b) shows a section through the brass cup f containing the dissolution-tube system. This consists of a stainless-steel tube m containing a thin-walled Teflon tube n. After a vertical part, the steel and Teflon tubes (m, n) are formed into spirals. The end of the steel spiral is sealed with a steel plug at l. The Teflon tube ends a few mm before the plug. The i.d. of the steel tube is 1.8 mm and that of the Teflon tube is 1.0 mm. Its wall thickness is 0.1 mm. The total length of the steel and Teflon spirals is about 400 mm.

A nozzle r made from stainless steel is tin-soldered at t to the steel tube m. The narrow part of the nozzle is tightly attached to the Teflon tube. The upper part of the nozzle fits the end of the inner glass tube b, which is enclosed by a short brass tube s. An epoxy seal is made between the brass tube, the glass, and the steel tube. A 1 mm steel tube leads from the T-junction at k to the bottom of the brass cup, where it forms a second spiral which leads to the annular space between the two glass tubes b and c. An epoxy seal is made at q.

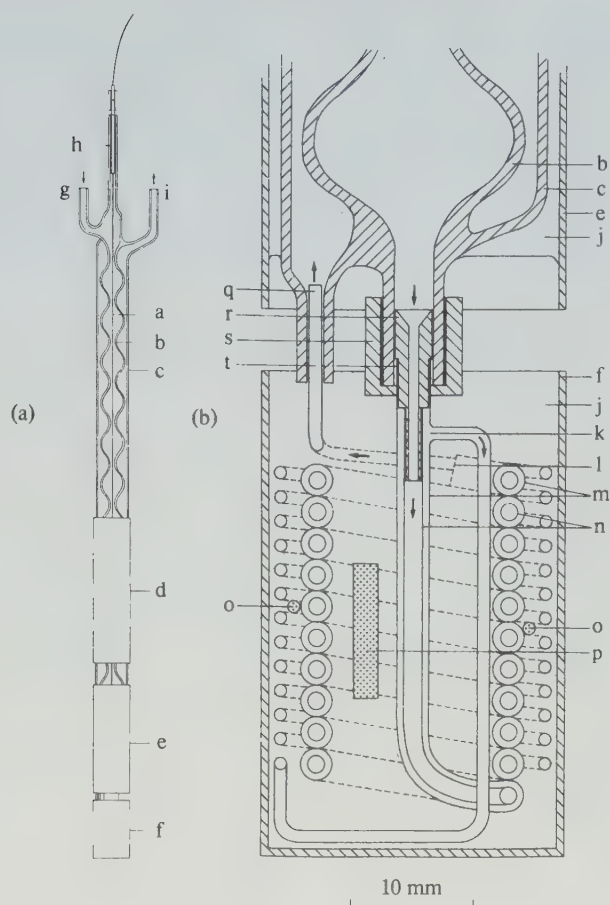


FIGURE 1. (a), Calorimetric vessel for dissolution of small quantities of easily or slightly soluble liquids. a, Steel tube attached to a Hamilton syringe; b, c, concentric glass tubes; d, e, brass tubes; f, brass tube containing the dissolution vessel; g, solvent inlet; h, steel tube fixed to the central glass tube; i, solvent outlet. (b), Section through the lower part of the vessel. j, Wood's-metal filling; k, T-junction; l, end of steel spiral; m, stainless-steel tube; n, Teflon tube; o, p, calibration heaters; q, connection to solvent outlet from the reaction vessel; r, nozzle; s, brass tube; t, tin-soldered connection between the nozzle and the stainless-steel tube.

The space between the spiral system and the brass cup is filled with Wood's metal. Two $50\ \Omega$ calibration heaters (o and p) are imbedded in the Wood's metal. The heater p is a standard metal film resistor (Vitrom 471). Heater o was made from 0.05 mm lacquered and nylon-spun manganin wire and was inserted into a thin-walled Teflon tube (length about 50 mm) which was wound around the steel-tube spiral system as indicated by the figure. Both heaters were fitted with two terminal copper leads (diameter 0.2 mm) enclosed by thin-walled Teflon tubes (wall thickness 0.1 mm), which were flattened around the copper leads so as to ensure good thermal contact with the surrounding Wood's metal. So as to equilibrate the leads further, about 100 mm of their length was imbedded in the upper part of the cup. The leads

were then carried out through the space between the glass tube c and the brass tubes d and e. The resistance of those parts of the copper leads which were imbedded in the brass cup f was considered to be part of the calibration heater.

During an experiment, a constant flow of solvent is sucked through the vessel by a peristaltic pump (LKB Perpex). The flow enters the vessel at g (figure 1a), passes through the inner glass tube b, and enters the dissolution spiral tubes through the nozzle r, from which it is carried over to the Teflon tube n. At the end of the spiral l, the solvent flow will turn back through the annular space between the Teflon and

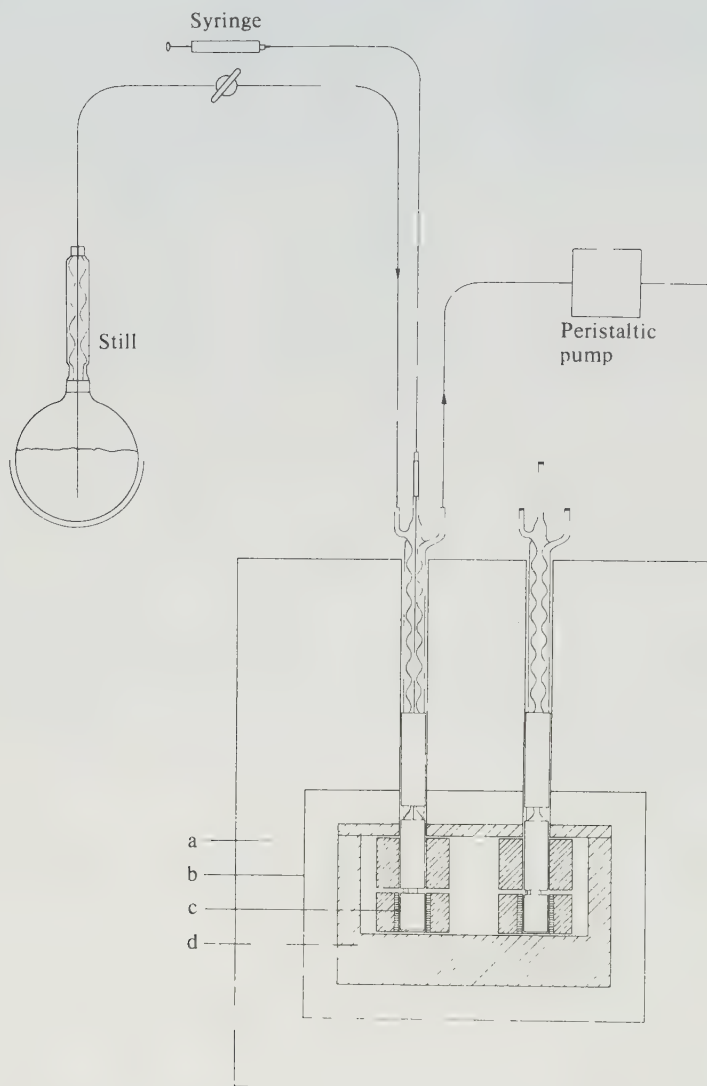


FIGURE 2. Experimental arrangement. a, Water thermostat; b, steel container; c, thermocouple plates; d, main heat sink.

the steel tubes. Following the vertical part of the tubes, the flow passes through the T-junction *k* to the narrow steel tube and is delivered to the space between glass tubes at *q*. The flow will leave the vessel at *i*.

The solute is introduced to the dissolution zone by means of a thin steel tube *a* (length 1 m, i.d. 0.15 mm) fastened by epoxy to a Hamilton 100 mm³ gas-tight syringe (1710 LT). The tube ends in the vertical part of the Teflon tube *n*, about 30 mm from the top of the dissolution vessel.

Seals at *g* and *i* (figure 1a) between the glass vessel and the stainless-steel flow lines are made by short-length silicone-rubber tubing. A short outer tube is soldered around the injection needle *a* and acts as a stop against the steel tube *h*. This latter tube is permanently fixed by epoxy to the inlet tube of the glass vessel. A piece of silicone-rubber tubing forms the seal between the outer tube of the injection needle and the tube *h*; compare reference 3.

The overall calorimetric setup is shown schematically in figure 2. The calorimeter⁽⁴⁾ has two identical units contained in a metal block *d* serving as the main heat-sink, which is suspended inside a steel container *b*, positioned in a water thermostat *a* (± 0.001 K). Heat-flow sensors consist of semi-conducting thermocouple plates *c*. The reference vessel can be identical with the reaction vessel or it can have a slightly different design.

So as to avoid formation of gas bubbles in the solvent (water) flow, it was taken from a gently boiling source.⁽³⁾

The syringe drive is the same as was used earlier.⁽¹⁾ So as to reduce solute diffusion from the steel tube *a*, its inner diameter, 0.15 mm, has been made smaller compared with the earlier instrument.⁽¹⁾ Leakage of solute through the Teflon tip of the syringe plunger (or, possibly, between the Teflon tip and the glass wall) was shown to be significant for some solutes. To reduce this effect a mercury seal was introduced; see figure 3. The steel rod of the plunger was thinned down over a length of about 4 mm at *d* and a small glass funnel *c* was attached to the end of the syringe by means of epoxy resin. The mercury seal is produced in the following way:

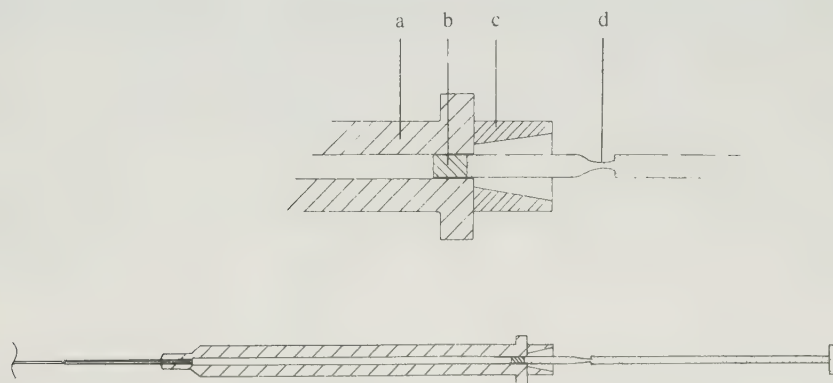


FIGURE 3. Modified Hamilton syringe. *a*, Barrel; *b*, Teflon tip; *c*, glass funnel; *d*, cavity in the plunger.

after the syringe has been filled with liquid the plunger is pushed into the barrel until the thinner part is in the lower end of the glass funnel; any liquid in the funnel is blown away with dry air and a small amount of mercury is introduced into the funnel; when the plunger is pushed further into the barrel the mercury will form a seal in the space between the steel rod and the glass; the excess mercury in the funnel is poured off before inserting the syringe into the syringe drive.

Electronic units used for amplification, recording, and calibration were of the same type as used with the gas calorimeter.⁽³⁾ The curve of output potential against time was integrated by use of a desk-top computer (ABC 80, Luxor, Sweden) and was also monitored by a potentiometric recorder. The computer was programmed to regulate switching times for the syringe drive and the calibration heater and for integration and other calculations.

EXPERIMENTAL PROCEDURES

The rate of solvent flow is usually about $10 \text{ mm}^3 \cdot \text{s}^{-1}$ and the volume of solute injected is normally in the range of 1 to 10 mm^3 . For easily soluble compounds and for volatile compounds at least two different quantities are injected, usually 1 to 2 mm^3 and 8 to 10 mm^3 , respectively. This was done so as to be able to correct for diffusion and leakage effects (see Section 3). Integration times are typically 80 to 120 min. The time between the end of one injection period and the beginning of the next is kept constant for each compound so as to arrive at the same "diffusion state" (see Section 3). Injection rates were usually $\leq 3 \times 10^{-12} \text{ m}^3 \cdot \text{s}^{-1}$, leading to a final solute concentration which can often be considered as infinite dilute ($< 5 \text{ mol} \cdot \text{m}^{-3}$). For slightly soluble compounds, the volumes injected are normally in the range 2 to 5 mm^3 and integration periods are typically in the range of 2 to 6 h.

MATERIALS

Methanol and butan-1-ol (B.D.H., Aristar), ethanol (Kemetyl AB Produkter), and propan-1-ol (B.D.H., AnalaR) were dried by refluxing over CaH_2 for 3 to 5 h and were then fractionally distilled. Benzene (B.D.H., AnalaR) was dried over A4 molecular sieves for several hours and was then fractionally distilled.

For all samples the mass fraction of water was ≤ 0.0002 as determined by g.l.c. As judged by g.l.c. the purities were ≥ 99.8 moles per cent for the alcohols and ≥ 99.5 moles per cent for benzene.

1,2-Ethanediol ("Fluka Garantie") was used without further purification. Reagent-grade water produced by a Milli-Q filtration system was used in the calorimetric experiment.

CALCULATIONS

Molar enthalpies of solution were calculated from the equation:

$$\Delta_{\text{sol}} H_{\text{m}} = -\varepsilon A/n, \quad (1)$$

where ε is the calibration constant, A is the potential-time integral, and n is the amount of solute injected. Values of n were calculated from

$$n = (\rho/M)(dV/dt)t, \quad (2)$$

where ρ is the density of the solute at the temperature of the syringe holder (usually thermostatted at 298 K), dV/dt is the volume displacement rate by the syringe, t is the injection time, and M is the molar mass. Values for dV/dt were determined by weighing water displaced by the syringe drive at various rates over a measured interval of time.

For easily soluble compounds, a significant diffusion of solute can take place from the tip of the syringe needle. This problem can be handled in different ways as discussed below.

3. Results and discussion

APPEARANCE OF CURVES OF POTENTIAL DIFFERENCE AGAINST TIME

Figures 4 and 5 show some typical curves of potential difference U against time t . Figure 4 shows the result of two injections of propan-1-ol into water using different injection times but the same injection rate, about $2.8 \times 10^{-12} \text{ m}^3 \cdot \text{s}^{-1}$. The first injection (600 s) corresponds to the delivery of about 1.7 mm^3 of propan-1-ol resulting in an enthalpy change of 220 mJ. The second injection (8.3 mm^3) will lead to steady-state conditions. When easily soluble compounds like propan-1-ol are injected at a rate which is much less than the rate of the solvent flow, it can be assumed that the solution formed in the dissolution zone has a well-defined concentration. It is then possible to arrive at different well-defined final solute concentrations by variation of the injection rate or of the solvent flow.

Figure 5 shows typical curves resulting from the injection of 5 mm^3 of benzene into water. When the dissolution vessel has been used for some time (weeks) the

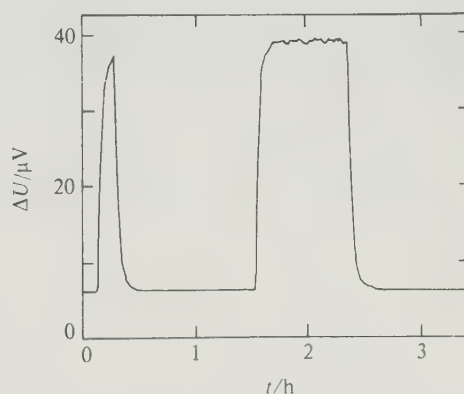


FIGURE 4. Curves of potential difference against time for solution of propan-1-ol in water. Sample injection rate was about $2.8 \times 10^{-12} \text{ m}^3 \cdot \text{s}^{-1}$ and the injection time 600 and 3000 s, respectively. Water flow rate was $11 \text{ mm}^3 \cdot \text{s}^{-1}$.

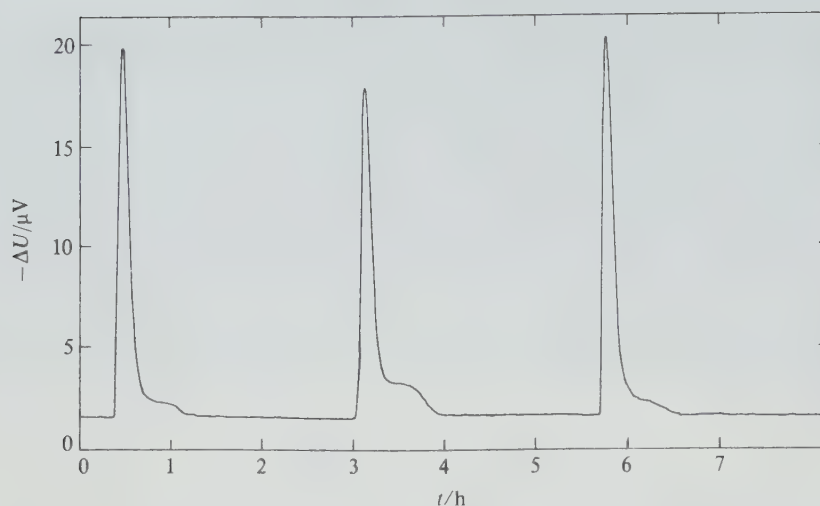


FIGURE 5. Typical curves of potential difference against time for solution of benzene in water. Injection rate was about $28 \times 10^{-12} \text{ m}^3 \cdot \text{s}^{-1}$ and the injection time was 180 s. Water flow rate was $11 \text{ mm}^3 \cdot \text{s}^{-1}$.

peaks become less sharp and it will take much longer before the signal returns to the baseline. Presumably this behaviour is due to a change in the surface properties of the Teflon which leads to a decreased ability of the hydrocarbon to form a film of large surface area in the Teflon tube. The original properties of the vessel can be restored by pumping a KOH in (water + ethanol) solution through the vessel (10 g of KOH dissolved in 100 cm^3 of 50 volume per cent water + ethanol). We have found such behaviour to be typical for all types of Teflon-tube vessels we have tested during the course of this work, including the original design.⁽¹⁾

For slightly soluble compounds the concentration of solute in the solution will vary with the time of the experiment. Such measurements will thus not lead to well-defined values for concentration of solute. However, in these cases largest concentrations will usually be low enough to regard solutions as infinitely dilute.

ELECTRICAL CALIBRATION EXPERIMENTS

We have earlier shown that significant systematic errors can easily be introduced by electrical calibrations of flow vessels used with heat-conduction calorimeters.⁽³⁾ The vessel described here was fitted with two different types of heaters (o and p, figure 1b). Heater p is considered as the regular calibration heater. It is imbedded in Wood's metal and is positioned close to the main dissolution zone. To test the accuracy of the electrical calibration procedure, solution experiments with propan-1-ol in water were performed at 298.15 K. Propan-1-ol was chosen as a test substance because its $\Delta_{\text{sol}}H_{\text{m}}$ value is accurately known at low concentrations and diffusion effects are not very large (see below). Two essentially identical solution vessels were used with different but very similar calorimeters. Results are

TABLE 1. Results of test experiments with different calibration heaters (o, p) and determination of molar enthalpies of solution $\Delta_{\text{sol}}H_{\text{m}}$ of propan-1-ol in water at 298.15 K. Final concentration of propan-1-ol = $0.003 \text{ mol} \cdot \text{dm}^{-3}$. Water flow rate was $11 \text{ mm}^3 \cdot \text{s}^{-1}$. Uncertainties are twice the overall standard deviation of the mean. ε is the electrical calibration constant and N is the number of experiments

Calibration heater	Vessel 1				Vessel 2			
	N	$\varepsilon/(\text{W} \cdot \text{V}^{-1})$	N	$\Delta_{\text{sol}}H_{\text{m}}/(\text{kJ} \cdot \text{mol}^{-1})$	N	$\varepsilon/(\text{W} \cdot \text{V}^{-1})$	N	$\Delta_{\text{sol}}H_{\text{m}}/(\text{kJ} \cdot \text{mol}^{-1})$
o	5	11.07 ± 0.02	12	-10.28 ± 0.05	7	8.25 ± 0.02	11	-10.29 ± 0.04
p	8	10.97 ± 0.02	12	-10.19 ± 0.05	11	8.22 ± 0.02	11	-10.25 ± 0.04

summarized in table 1; $\Delta_{\text{sol}}H_{\text{m}}$ values were corrected for diffusion effects by the method described below.

For both vessels the regular heater gives a lower value of ε than heater o (0.9 and 0.4 per cent for vessels 1 and 2, respectively). This means that for the regular heaters larger fractions of the power evolved will pass the thermopile as compared with the heaters o. However, the differences between the two values of ε for each of the vessels are not as similar as one would expect from the values for the imprecision of the calibration experiments (table 1). From this we conclude that variations in design or position of the heaters can lead to differences in the values of ε amounting to at least 0.5 per cent; compare reference 3. The mean value for $\Delta_{\text{sol}}H_{\text{m}}$ arrived at by use of the regular heaters is $-(10.22 \pm 0.04) \text{ kJ} \cdot \text{mol}^{-1}$, which is 0.6 per cent lower than a value determined at this Laboratory⁽⁵⁾ by use of an LKB 8700 Precision Calorimeter: $\Delta_{\text{sol}}H_{\text{m}}^{\infty} = -(10.16 \pm 0.02) \text{ kJ} \cdot \text{mol}^{-1}$ (the uncertainty is an estimate). The difference is considered to be marginally significant.

With the present instrument, the electrical-calibration values can be determined automatically in connection with each series of measurements. This is valuable as the calibration constant is quite sensitive to changes in the solvent flow rate (about 0.4 per cent for a variation of $1 \text{ mm}^3 \cdot \text{s}^{-1}$). However, the the possibility of systematic errors in electrical-calibration values, it is believed that the accuracy obtained with the present type of dissolution calorimeter can often be improved if electrical-calibration values are empirically corrected by use of results obtained with well known test processes. Enthalpies reported below have been calculated by use of values of ε determined by the regular heaters, but they are empirically corrected using results obtained with the propan-1-ol test reaction. Corrections amount to 0.3 and 0.8 per cent for vessels 1 and 2, respectively.

DIFFUSION AND LEAKAGE PROBLEMS

The solute-delivery system used here allows for the precise injection of very small samples and is well suited to automatic-working procedures. The main problem involved is the risk of significant diffusion effects at the tip of the delivery tube and leakage of substance through the seal between the plunger and the barrel of the syringe. This latter problem has been dealt with successfully by use of the mercury

seal described in Section 2. The tendency for diffusion through the delivery tip is more difficult to overcome for applications like those described here.

Any diffusion effect which takes place in the dissolution zone of the calorimetric vessel will contribute to the instrument signal. If such effects take place only during the main period (the integration period) of an experiment, they should therefore not lead to any error in repeated measurements (the volume delivered during the first injection might not be representative for several reasons). However, if diffusion occurs during the fore and/or after periods, this will lead to false baseline values.

Diffusion of solute from the delivery tube will presumably be accompanied by diffusion of solvent into the tube. If water is used with a hygroscopic solute such diffusion can possibly cause problems even if the solute has a low tendency to diffuse. If extensive solvent diffusion should take place into the delivery tube, a temperature rise could possibly take place outside the calorimetric vessel. However, with the narrow delivery tube used here and with its tip positioned in the lower part of the tube *n* (figure 1b), the risk of this effect seems small, as demonstrated by the following experiments.

The syringe system was charged with dry propan-1-ol or methyl butanoate and the tip of the syringe needle was inserted for 2 h into a tube similar to the calorimetric vessel and filled with water. The syringe delivery tube was then taken up and the content was analysed for water by g.l.c. It was found that for both solutes the water concentration had not increased significantly after a point 15 mm from the tip of the delivery tube. This distance is well within the calorimetric zone of the vessel.

If a series of experiments is run with increasing time increments between the injections, the effect of leakage from the syringe will increase. For instance, in experiments with methyl acetate a 3 h time increment caused a decrease in the apparent $\Delta_{\text{sol}}H_m$ by about 5 per cent if no mercury seal was used. With the seal applied, the decrease in the apparent enthalpy was ≤ 1 per cent following a 3 h increment period. Also with other volatile compounds, such as benzene, results indicated that the mercury seal prevented leakage. For relatively non-volatile compounds such as butan-1-ol, the mercury seal was not used.

When the vessel is used for dissolution of an easily soluble compound such as methanol in water, a significant diffusion through the delivery tip will continue for a long time (hours) after the syringe drive has been switched off. For methanol as a solute, the calorimetric signal can appear essentially constant about 50 min after the injection period and might then be mistaken for the baseline. However, if water from the vessel is sucked into the syringe, a significant baseline shift takes place, being a measure of the power evolution due to diffusion. The rate of diffusion can be decreased by fitting the end of the delivery tube with a narrower end piece. However, we found this arrangement less practical as the end piece (i.d. 0.1 mm) frequently became clogged.

If only one injection is made per filling of the syringe (e.g. during a long steady-state experiment), the true baseline can be found after the experiment by sucking solvent into the syringe. A correct assignment of the integral of the potential

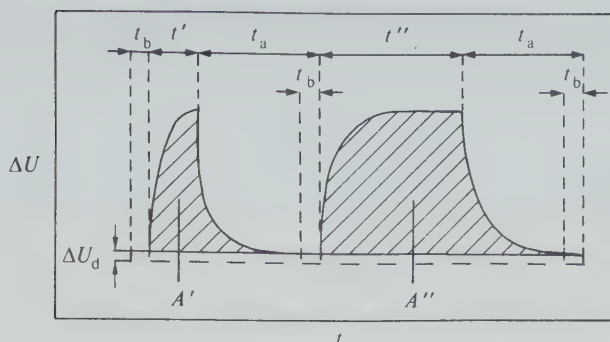


FIGURE 6. Schematic curves of potential difference against time for a solution experiment where significant diffusion takes place. A , the recorded integral; t , injection time; t_a , time between two consecutive injections; t_b , baseline period; ΔU_d potential difference between the recorded and the true baseline.

difference against time (or the power in case of a steady-state experiment) can thus be made even if significant diffusion takes place prior to the measurement. But usually one wishes to make measurements (automatically controlled) with each syringe filling, *e.g.* so as better to assess the precision of the measurements and to obtain values for several final concentrations of the solute. We have therefore adopted the following correction method which will account both for effects of diffusion in the solution vessel and for leakage effects through the seal in the syringe. The method requires that at least two injections are made and that the injected quantities are significantly different. Further, it is required that the rate of diffusion is the same at the end of each integration period, *i.e.* the apparent baseline value is, within uncertainty limits, the same before and after each injection. We believe that this condition is reached if the time between the end of one injection period and the start of the following injection is kept constant (t_a in figure 6).

Figure 6 shows schematically curves of potential difference against time for two experiments where diffusion takes place from the delivery tip: t is the injection time and t_a is the time between subsequent injections; A is the recorded area for an experimental period covering the time $(t + t_a - t_b)$; A is based on the mid-point (mean) values for the fore and after periods t_b . The A -value is thus expected to be lowered by the quantity $\Delta U_d(t + t_a)$.

If some solute is lost through a leak outside the dissolution vessel, this quantity will not contribute to the measured integral. Assuming that the leakage rate is constant, the loss can be accounted for by $\Delta U_l(t + t_a)$ where ΔU_l is the expected potential difference if the substance lost had been dissolved in the vessel. The corrected integral A_{corr} is thus

$$A_{\text{corr}} = A + (\Delta U_d + \Delta U_l)(t + t_a). \quad (3)$$

But

$$A_{\text{corr}} = k'n, \quad (4)$$

where k' is a constant and n is the total amount of solute leaving the delivery system during the time t in the case of no leakage effects. Combining equations (2) and (4) leads to

$$A_{\text{corr}} = kt, \quad (5)$$

where k is a constant for a series of repeated experiments. From equations (3) and (5) we obtain

$$A = \{k - (\Delta U_d + \Delta U_l)\}t - (\Delta U_d + \Delta U_l)t_a. \quad (6)$$

If A is plotted against t , a linear relation is obtained from which k can be derived.

TEST EXPERIMENTS

The calorimetric vessels described in this work have been used for the determination of enthalpies of aqueous solution at infinite dilution for normal alcohols (C_1 to C_8) over the temperature range 288.15 to 318.15 K. Measurements have also been made with several series of esters. Results from these studies will be reported in detail elsewhere. Here results will be given for measurements of the lower alcohols at 298.15 K, used as test experiments for the vessels. Results will also be given for measurements with benzene.

In table 2 results are summarized for solution measurements with methanol, ethanol, and butan-1-ol. Their final concentrations were 6.1, 4.2, and 2.7 mol $\cdot$ m $^{-3}$, respectively. These concentrations are low enough to enable us to regard the enthalpies of solution as identical to $\Delta_{\text{sol}}H_m^\infty$.^(5,6) The correction procedure outlined above was applied. Figure 7 shows results from a series of experiments with propan-1-ol using different injection times. From values for the slope and the intercept (see the insert figure) k is calculated, leading to values for the sum δ of diffusion and leakage rates. These values are also summarized in table 2. As expected the δ -values decrease in the order methanol > ethanol > (propan-1-ol or

TABLE 2. Results of solution experiments with some alcohols in water at 298.15 K. Two similar microcalorimetric vessels were used (1, 2); they were calibrated by means of solution of propan-1-ol in water. Each ΔH_m reported here is based on 8 to 10 measurements. Uncertainties are twice the overall standard deviation of the mean. δ is the rate of diffusion and/or leakage from the syringe; see text

	Vessel 1		Vessel 2		Literature values
	$-\Delta_{\text{sol}}H_m^\infty$ kJ $\cdot$ mol $^{-1}$	$10^{15}\delta$ m $^3 \cdot$ s $^{-1}$	$-\Delta_{\text{sol}}H_m^\infty$ kJ $\cdot$ mol $^{-1}$	$10^{15}\delta$ m $^3 \cdot$ s $^{-1}$	$-\Delta_{\text{sol}}H_m^\infty$ kJ $\cdot$ mol $^{-1}$
CH $_3$ OH	7.29 $\pm$ 0.04	9 $\pm$ 3	7.34 $\pm$ 0.03	14 $\pm$ 2	7.30 $\pm$ 0.02 ^a
C $_2$ H $_5$ OH	10.15 $\pm$ 0.05	7 $\pm$ 4	10.14 $\pm$ 0.04	12 $\pm$ 3	10.16 $\pm$ 0.02, ^a 10.15 $\pm$ 0.02 ^b
C $_3$ H $_7$ OH	—	4 $\pm$ 2	—	8 $\pm$ 3	10.16 $\pm$ 0.02 ^a
C $_4$ H $_9$ OH	9.32 $\pm$ 0.05	4 $\pm$ 6	9.31 $\pm$ 0.04	5 $\pm$ 2	9.27 $\pm$ 0.03 ^a

^a Values are based on results from reference 5 which have been slightly corrected for dilution effects by recent microcalorimetric experiments.⁽⁶⁾ Uncertainties are estimates.

^b Calculated from data of reference 8. Personal communication by K. N. Marsh.

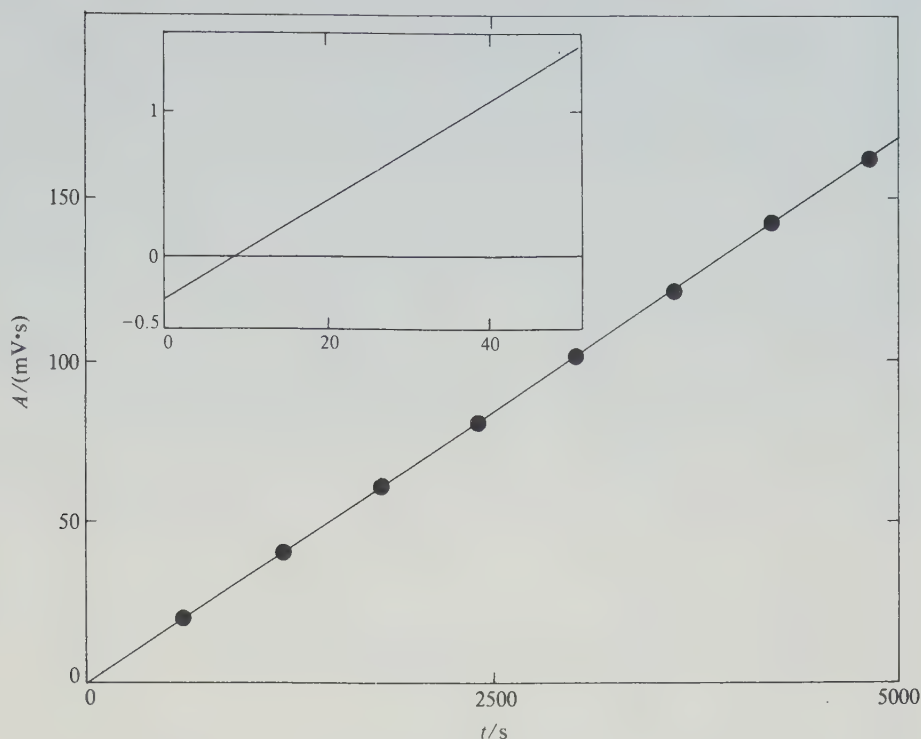


FIGURE 7. Recorded integral A plotted against injection time t for a series of solution experiments with propan-1-ol in water. Sample injection rate was $2.8 \times 10^{-12} \text{ m}^3 \cdot \text{s}^{-1}$ and the water flow rate was $11 \text{ mm}^3 \cdot \text{s}^{-1}$.

butan-1-ol). In the present work typically 2 to 8 mm³ of alcohol was injected in each experiment. For methanol and butan-1-ol the maximum correction terms amounted to 4 and 1 per cent, respectively, of the corrected value.

In table 2 are also given $\Delta_{\text{sol}}H_{\text{m}}^{\infty}$ values determined in this Laboratory by a well-established solution calorimetric technique⁽⁵⁾ (LKB Precision Calorimeter) and corrected to infinite dilution by flow-microcalorimetric dilution experiments.⁽⁶⁾ As discussed above, the value for propan-1-ol was used to correct slightly the electrical calibration value determined for the present microcalorimetric vessels. It is seen that the results obtained with the two microcalorimetric vessels are identical within uncertainty limits and are in full agreement with the macrocalorimetric results.

During the course of this work a large series of dissolution measurements with benzene was made. With the different instrument models tested we have consistently obtained slightly more positive values at 298.15 K as compared with the value reported earlier: $\Delta_{\text{sol}}H_{\text{m}} = (2.08 \pm 0.04) \text{ kJ} \cdot \text{mol}^{-1}$. The mean value obtained with the instrument described here is $\Delta_{\text{sol}}H_{\text{m}} = (2.22 \pm 0.02) \text{ kJ} \cdot \text{mol}^{-1}$.

To test another solvent than water we injected butan-1-ol into a stream of 1,2-ethanediol at 288.15 and 298.15 K. The obtained values for $\Delta_{\text{sol}}H_{\text{m}}^{\infty}$ were

$(3.39 \pm 0.02) \text{ kJ} \cdot \text{mol}^{-1}$ and $(3.49 \pm 0.01) \text{ kJ} \cdot \text{mol}^{-1}$, respectively, in full agreement with those obtained earlier in this Laboratory.⁽⁷⁾

Thus, the present solution-calorimetric technique can be used with very small quantities of liquid solutes, which may be easily soluble or (for water as solvent) very slightly soluble. For easily soluble compounds the precision approaches the level reached by the very precise macrocalorimetric instruments but the amount of solute used is typically 50 to 100 times less. The solution vessel works without gas phase and can therefore be used with very volatile solutes and solvents. A very high dilution factor can be used which often will lead to final concentrations low enough to be regarded as infinitely dilute. The syringe technique used is simple and avoids many of the problems connected with the inclusion of a sample in an ampoule. Further, the technique of injection of the sample into a flow of solvent makes it possible to make the measurement and calculation procedures automatic.

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REFERENCES

1. Gill, S. J.; Nichols, N. F.; Wadsö, I. *J. Chem. Thermodynamics* **1975**, 7, 175.
2. Gill, S. J.; Nichols, N. F.; Wadsö, I. *J. Chem. Thermodynamics* **1976**, 8, 445.
3. Gill, S. J.; Wadsö, I. *J. Chem. Thermodynamics* **1982**, 14, 905.
4. Wadsö, I. *Science Tools* **1974**, 21, 18.
5. Rothschild, W. J. Thesis, University of Minnesota, **1981**.
6. Hallén, D.; Nilsson, S.-O.; Wadsö, I. Unpublished.
7. Nwankwo, S.; Wadsö, I. *J. Chem. Thermodynamics* **1980**, 12, 881.
8. Costigan, M. J.; Hodges, L. J.; Marsh, K. N.; Stokes, R. H.; Tuxford, C. W. *Aust. J. Chem.* **1980**, 33, 2103.

II

A flow microcalorimetric vessel for solution of slightly soluble
solids

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Abstract

A flow-calorimetric vessel has been designed for the determination of enthalpies of solution for slightly soluble solids with particular reference to water as a solvent. The design has been chosen to fit a commercial calorimetric system (2277 multichannel microcalorimeter system, LKB Products, Bromma, Sweden). At each experiment the ampoule is charged with 1 to 10 mg of the solid substance. The instrument has been tested by solution of acetanilide and adenine in water in the temperature ranges 288 to 310 K and 288 to 318 K, respectively.

1. Introduction

Calorimetric determination of enthalpies of solution forms an important technique for characterization of solute-solvent interactions. To a significant extent such measurements are currently concerned with aqueous systems, often in connection with problems of importance for biochemical systems. Measurements are then mainly conducted with rather simple biochemical substances such as amino acids, peptides, nucleotide bases, sugars, etc. Of major importance in this connection is the large number of studies performed on "model compounds", i.e. simple organic compounds which are thought to mimic some details of solute-solvent interactions in complex biological systems, e.g. hydrophobic hydration.⁽¹⁻³⁾ From an experimental point of view such studies are often made difficult by low solubilities. Further, many substances which would be interesting to study in these connections cannot easily be obtained in quantities normally required in solution calorimetry. For these reasons we have developed in our laboratory a series of flow microcalorimetric solution vessels used with twin heat conduction calorimeters. They include vessels for gaseous⁽⁴⁾ or liquid^(5,6) solutes. Some years ago Gill and Seibold⁽⁷⁾ reported the design of a microcalorimetric flow vessel of the same general type, but designed for use with slightly soluble solids. The sample, which was contained in a glass capillary tube, was protected by an air space from premature contact with the solvent. More recently a corresponding flow solution vessel was built in our laboratory.⁽⁸⁾ In that design the sample was contained in a small cavity where it was covered with saturated solution. After equilibration a flow of pure solvent was brought in contact with the sample. This instrument proved to have some shortcomings and was never reported in any detail. Using the same principle, the instrument has now been redesigned. The new

construction is based on a microcalorimetric "perfusion and titration vessel" which was recently developed in our laboratory⁽⁹⁾ as part of our 4-channel microcalorimetric system.⁽¹⁰⁾ The new solution vessel has been tested by dissolution of adenine and acetanilide in water at different temperatures.

2. Experimental

APPARATUS

Figure 1A shows schematically a twin calorimeter which forms one of the "channels" in the 4-calorimeter system. In the experiments reported here the commercial version (2277 multichannel microcalorimeter system, LKB Produkter, Bromma, Sweden) of the system was used. The twin calorimeter, which is positioned in a precisely thermostated water bath d ($\pm 10^{-4}$ K) contains a reference vessel c and the insertion vessel used for the solution measurements b . This vessel, shown in some detail in figures 1B and 1C, is the perfusion version of the vessel described earlier.⁽⁹⁾ The regular stirrer used with that vessel was replaced with a dissolution ampoule m , shown in more detail in figure 2. It consists of a steel cylinder e , f , diameter 8 mm, which can be attached to the regular stirrer shaft a through a close fit to the inlet tube of the ampoule b , which is connected to the screw lid of the ampoule e . The inner diameter of the inlet tube b is narrowed down to 1 mm as it passes through the lid. The diameter of the cavity g in the cylinder f is 4 mm, leaving a 1 mm space to the inlet tube. The upper part of the cavity is in contact with two short steel tubes d , which are connected to Teflon tubes c (not shown in figure 2B). During a measurement the Teflon tubes are pressed into vertical scores h cut into the ampoule wall.

All parts of the calorimetric vessel which come in contact with the chemical substances are made from acid-proof steel or Teflon.

MEASUREMENT PROCEDURE

The dissolution ampoule is charged with 1 to 10 mg of solid substance. The sample is pressed with a steel pestle against the bottom of the cavity of the ampoule until it forms a thin attached layer. Remaining loose particles and dust are blown away by dry air before the mass of the sample is determined by differential weighing of the cylinder f. The cavity g is filled with saturated solution and the screw lid e is attached to the cylinder f, after which a saturated solution is slowly forced through the ampoule (by use of a syringe connected to the inlet tube) until all air has been replaced by solution. The stirrer shaft is filled with degassed solvent and connected to the ampoule without enclosing any air into the flow system. The Teflon tubes c are then pressed into the scores in the cylinder. The sample cup of the perfusion vessel b in figure 1 is partly filled with degassed solvent and the vessel assembly is sealed by use of its bayonet connection and a Teflon ring.⁽⁹⁾ Remaining air in the vessel is replaced by solvent introduced through the titration tube e in figure 1 and the outlet of this perfusion vessel is connected to a peristaltic pump (LKB Perpex), compare figure 1A. The vessel is introduced stepwise⁽⁹⁾ to the measurement position in the twin calorimeter, figure 1A. A closed ampoule charged with 4 cm³ water was used as a reference vessel. After equilibration for about 2 h the stirrer and the peristaltic pump (figure 1) are started. The solvent flow rate through the vessel is normally kept at 6 mm³·s⁻¹. Electrical calibrations were performed by use of an insertion heater⁽⁹⁾ positioned in the sample cup 1, figure 1c. A microprocessor was used for the integration of voltage-time curves and for regulation of the electrical switching times. Degassed solvent was obtained from a gently boiling source, figure 1A.

MATERIALS

Adenine (SERVA, analytical grade, synthetic, 99.5 moles per cent) and acetanilide (BDH, OAS-grade, better than 99.5 moles per cent) were used as received. Reagent-grade water was produced by a Milli-Q filtration system.

CALCULATIONS

There is no stirring and no liquid flow during the initial period of the measurement and there will thus be a small difference between the initial baseline value $U(i)$ and the final value $U(f)$. Starting with Tian's equation (1):

$$P = \epsilon U + \epsilon \tau (dU/dt) \quad (1)$$

where P is the thermal power developed in the vessel, ϵ is the calibration constant, U is the recorded potential, τ is the time constant and dU/dt is the time derivative of the potential signal, integration over time leads to equation (2):

$$\Delta H_{\text{exp}} = - \epsilon A - \epsilon \tau [U(f) - U(i)], \quad (2)$$

where ΔH_{exp} is the enthalpy change and A the recorded voltage-time integral in the calorimetric experiment. $\epsilon\{U(f) - U(i)\}$ is about $2 \mu\text{W}$ and with $\tau \approx 100 \text{ s}$, the contribution to ΔH_{exp} from the second term in equation (2) is then about 0.2 mJ , which is negligible in these measurements. For the calculation of the molar enthalpy of solution $\Delta_{\text{sol}} H_{\text{m}}$ two correction terms should be considered: contributions from processes in the ampoule before the calorimetric measurements starts and initial dilution effects. If the measurement temperature is different from the room temperature, a certain amount n' of substance will be expected to dissolve or to crystallize in the ampoule. The

equilibration time is kept constant and the contact area between the solid sample and the liquid will be essentially the same in all experiments. Therefore, for each measurement temperature n' will be considered as a constant.

For some compounds there might be a significant effect at the start of the measurement from dilution of the saturated solution initially contained in the ampoule, $\Delta_{dil}H$. If the ampoule is charged with n mol of sample we will thus have:

$$\Delta H_{exp} = n\Delta_{sol}H_m - n'\Delta_{sol}H_m + \Delta_{dil}H. \quad (3)$$

A plot of ΔH_{exp} against n will give $\Delta_{sol}H_m$ as the slope and the sum of the two correction terms as the intercept.

The method is intended for use with slightly soluble compounds and the two correction terms in equation (3) can thus be expected to be small. The concentration of the solution leaving the calorimetric vessel is not well defined. However, it will normally be much lower than the saturation concentration. Therefore, in many cases the $\Delta_{sol}H_m$ value can be assumed to be insignificantly different than the value at infinite dilution $\Delta_{sol}H_m^\infty$ and thus:

$$\Delta_{sol}H_m^\infty \approx 1/n \Delta H_{exp}. \quad (4)$$

3. Results and discussion

Figure 3 shows a typical calorimetric record from a solution experiment with 8.63 mg of acetanilide at 298.15 K. The right-hand scale in figure 3 shows the solute molality as calculated from the derived $\Delta_{sol}H_m$ value (no dynamic correction was applied; the time

constant of the instrument was about 100 s). The maximum value is 7 per cent of the solubility value $47 \text{ mmol}\cdot\text{kg}^{-1}$.⁽¹¹⁾ Approximately the same "dissolution efficiency" was found at the higher temperature.

For adenine the dissolution process was slightly less efficient. The maximum solute concentration was about 5 per cent of the solubility at 298.15 K.

The experimental results from the dissolution experiments are summarized in tables 1 and 2. In figures 4 and 5 ΔH_{exp} is plotted against n . From the linear relation slopes and intercepts in equation (3) are calculated. The derived quantities are summarized in table 3. It is seen that the intercepts in all cases are small and the $\Delta_{\text{sol}}H_m$ values are influenced only marginally. Table 3 also shows some $\Delta_{\text{sol}}H_m$ values from earlier experimental work. For acetanilide Logan⁽¹¹⁾ has reported solubility values over the temperature range 273 to 343 K. From these data corresponding $\Delta_{\text{sol}}H_m$ values were calculated for the three temperatures of the present calorimetric experiments. It is seen that there is good agreement at 288 K, whereas the calculated values become increasingly larger than the calorimetric results at the higher temperatures.

Kilday⁽¹²⁾ has performed a very careful and extensive study of the enthalpy of solution of adenine in water using an adiabatic solution calorimeter (about 200 mg of sample was dissolved in 300 cm^3 of water). Values were reported for five different commercial samples of analytical grade which were used without further purification. The mean value at 298.15 K listed in table 3 is in good agreement with the present results and the measurements refer to comparable conditions. The results from Kilday's measurements were corrected with $1.5 \text{ kJ}\cdot\text{mol}^{-1}$ to infinite dilution. As in the present work, no

correction was applied for the water content of the commercial samples; this was measured as about 0.15 per cent by mass. In the present work the final concentration of solute varies during the experiment and with the experimental temperature. However, using estimates of average concentration values and the dilution coefficient value $-316 \text{ kJ}\cdot\text{mol}^{-1}\cdot(\text{mol}\cdot\text{kg})^{-1}$ obtained by Kilday,⁽¹²⁾ corrections to infinite dilute solutions will be approximately 0.03 $\text{kJ}\cdot\text{mol}^{-1}$ (288.01 K), 0.05 $\text{kJ}\cdot\text{mol}^{-1}$ (298.15 K), 0.07 $\text{kJ}\cdot\text{mol}^{-1}$ (308.15 K) and 0.13 $\text{kJ}\cdot\text{mol}^{-1}$ (318.14 K). These dilution enthalpies are small and approximate and will be neglected. Thus for the present adenine values in table 3 $\Delta_{\text{sol}}H_m$ will be taken as equal to $\Delta_{\text{sol}}H_m^\infty$.

Kilday also reported a value $\Delta_{\text{sol}}H_m^\infty = (33.47 \pm 1.00) \text{ kJ}\cdot\text{mol}^{-1}$ at 298.15 K for a sample which had been further purified. This value includes a correction of 0.91 $\text{kJ}\cdot\text{mol}^{-1}$ for the water content which was 0.40 per cent by mass. If the corresponding correction is applied to our value, assuming a water content of 0.15 per cent by mass , $\Delta_{\text{sol}}H_m^\infty = (33.03 \pm 0.70) \text{ kJ}\cdot\text{mol}^{-1}$ is obtained.

Kilday⁽¹²⁾ found a significant increase in the solution enthalpy for adenine with decreasing sample particle size. This observation could not easily be tested with our measurement method. However, in a separate series of experiments, which will not be reported in detail, small pieces were cut from an adenine tablet and placed at the bottom of the sample container. The tablets had been prepared using a much higher pressure than that applied in the normal sample preparation. The dissolution time was longer than with the normal procedure, but the $\Delta_{\text{sol}}H$ values were not significantly different.

In table 3 a calorimetric value by Kanbour et al.⁽¹³⁾ for adenine

at 298.15 K is also given. This value is significantly lower than Kilday's and our values. Table 4 shows heat capacities derived from the present measurements. Dilution values were considered insignificant. Partial molar heat capacities of the solutes at infinite dilution $C_{p,2}^{\infty}$ were derived from:

$$C_{p,2}^{\infty} = \Delta_{\text{sol}} C_{p,m}^{\infty} + C_{p,m}^{\star} \quad (5)$$

where $C_p^{\star}$ is the heat capacity for the pure compound. For acetanilide $C_p^{\star}$ was determined by use of our micro drop heat capacity calorimeter,⁽¹⁴⁾ $\Delta T = 10$ K, $T_{\text{mean}} = 298.2$ K. Our value for $\Delta_{\text{sol}} C_{p,m}^{\infty}$ is lower than the value obtained by Kilday,⁽¹²⁾ $(79 \pm 10) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, but is not significantly different. However, $\Delta_{\text{sol}} C_{p,m}^{\infty} = (220 \pm 70) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ reported by Kanbour et al.⁽¹³⁾ is much higher than both of these determinations.

REFERENCES

1. Tanford, C. The Hydrophobic Effect: Formation of Micelles and Biological Membranes. 2nd edition. Wiley-Interscience: New York. 1980.
2. Franks, F. Biochemical Thermodynamics. Jones, M. N.: editor. Chapter 2. Elsevier: Amsterdam. 1979.
3. Wadsö, I. Pure Appl. Chem. 1983, 55, 515.
4. Gill, S. J.; Wadsö, I. J. Chem. Thermodynamics 1982, 14, 905.
5. Gill, S. J.; Nichols, N. F.; Wadsö, I. J. Chem. Thermodynamics 1975, 7, 175.
6. Nilsson, S.-O.; Wadsö, I. J. Chem. Thermodynamics 1984, 16, 317.
7. Gill, S. J.; Seibold, M. L. Rev. Sci. Instrum. 1976, 47, 1399.
8. Wadsö, I. Proc. 2nd Australian Thermodynamic Conference, Royal Austr. Chem. Inst. Melbourne. 1981.
9. Görman Nordmark, M.; Laynez, J.; Schön, A.; Suurkuusk, J.; Wadsö, I. J. Biochem. Biophys. Methods 1984, 10, 187.
10. Suurkuusk, J.; Wadsö, I. Chemica Scripta 1982, 20, 155.
11. Logan, T. S. J. Am. Chem. Soc. 1945, 67, 1182.
12. Kilday, M. V. J. Res. Nat. Bur. Stand. 1978, 83, 347.
13. Kanbour, F. I.; Ahmed, J. K.; Derwish, G. A. W. J. Solution Chem. 1983, 12, 763.
14. Suurkuusk, J.; Wadsö, I. J. Chem. Thermodynamics 1974, 6, 667.

TABLE 1. Corresponding enthalpy changes ΔH_{exp} and the number n of moles for dissolution of acetanilide in water at different temperatures (see the text)

T/K:		288.01		298.15		310.15	
$n/\mu\text{mol}$	$\Delta H_{\text{exp}}/\text{J}$	$n/\mu\text{mol}$	$\Delta H_{\text{exp}}/\text{J}$	$n/\mu\text{mol}$	$\Delta H_{\text{exp}}/\text{J}$	$n/\mu\text{mol}$	$\Delta H_{\text{exp}}/\text{J}$
11.44	0.174	15.05	0.269	17.71	0.365		
17.72	0.264	15.31	0.269	19.86	0.405		
21.80	0.334	24.46	0.440	21.12	0.438		
23.72	0.357	26.37	0.476	54.19	1.158		
27.31	0.405	63.85	1.153	64.67	1.366		
54.15	0.828	65.05	1.174	73.43	1.561		
54.62	0.848	65.92	1.190	74.81	1.585		
58.26	0.895						
59.41	0.895						
64.20	0.982						

TABLE 2. Corresponding enthalpy changes ΔH_{exp} and the number n of moles for dissolution of adenine in water at different temperatures (see the text)

T/K: 288.01		298.15		308.15		318.14	
$n/\mu\text{mol}$	$\Delta H_{\text{exp}}/\text{J}$	$n/\mu\text{mol}$	$\Delta H_{\text{exp}}/\text{J}$	$n/\mu\text{mol}$	$\Delta H_{\text{exp}}/\text{J}$	$n/\mu\text{mol}$	$\Delta H_{\text{exp}}/\text{J}$
0.79	0.020	1.49	0.018	1.41	0.033	0.74	0.05
2.93	0.078	6.62	0.177	2.65	0.074	6.40	0.198
3.09	0.084	7.26	0.208	7.29	0.221	6.69	0.204
4.59	0.140	20.00	0.634	7.59	0.241	7.63	0.227
10.92	0.346	21.75	0.669	34.71	1.129	25.08	0.802
12.88	0.409	21.75	0.672	35.08	1.145	50.14	1.667
18.13	0.584	30.27	0.963	36.26	1.184	52.47	1.749
21.00	0.671	30.79	0.969			53.76	1.812
21.65	0.680						

TABLE 3. Coefficients in equation (3) calculated from data in

tables 1 and 2 and literature $\Delta_{\text{sol}}H_{\text{m}}$. Uncertainties given for the present results are twice the standard deviation of the mean and uncertainties for $\Delta_{\text{sol}}H_{\text{m}}^{\infty}$ include estimates for impurities and calibration of 1 per cent.

Solute	T/K	$(\Delta_{\text{dil}}H - n'\Delta_{\text{sol}}H_{\text{m}})/\text{J}$	$\Delta_{\text{sol}}H_{\text{m}}^{\infty}/(\text{kJ}\cdot\text{mol}^{-1})^{\text{a}}$	$\Delta_{\text{sol}}H_{\text{m}}/(\text{kJ}\cdot\text{mol}^{-1})^{\text{b}}$
Acetanilide	288.01	-0.006 ± 0.012	15.40 ± 0.31	15.6^{c}
	298.15	-0.005 ± 0.004	18.13 ± 0.20	19.7^{c}
	310.15	-0.016 ± 0.011	21.45 ± 0.30	24.2^{c}
Adenine	288.01	-0.011 ± 0.008	32.37 ± 0.64	$32.3^{\text{d}} \quad 29.7 \pm 0.7^{\text{e}}$
	298.15	-0.033 ± 0.012	32.68 ± 0.66	
	308.15	-0.014 ± 0.005	33.00 ± 0.38	
	318.14	-0.026 ± 0.014	33.88 ± 0.54	

^a This work

^b Literature values

^c van't Hoff values from solubility measurements reported in reference 11.

^d Mean value from calorimetric measurements of five adenine samples reported in reference 12. $\Delta_{\text{sol}}H_{\text{m}} = \Delta_{\text{sol}}H_{\text{m}}^{\infty}$

^e Calorimetric value reported in reference 13. $\Delta_{\text{sol}}H_{\text{m}} = \Delta_{\text{sol}}H_{\text{m}}^{\infty}$

TABLE 4. Heat capacities at 298.15 K. Uncertainties are twice the standard deviation of the mean.

Compound	$C_p^*/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$	$\Delta_{\text{sol}}C_{p,m}^\infty/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$	$C_{p,2}^\infty/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$
Acetanilide	179.3 ± 0.3^a	273 ± 13	452 ± 13
Adenine	147.0 ± 1.0^b	48 ± 21	195 ± 21

^a Mean value from four series of 10 to 14 experiments.

^b Value taken from reference 12.

FIGURE LEGENDS

FIGURE 1. Microcalorimeter for solution of slightly soluble solids.

A. Section through the twin microcalorimeter a, with the perfusion vessel b and the reference vessel c. The calorimeter is immersed in a thermostated water bath d.

B. Picture of the perfusion vessel. Titration tube e, stirrer motor f, plastic tube g, steel tube h, brass bolts i, j, sample compartment k, l.

C. Sample compartment of the perfusion vessel with the dissolution ampoule m attached to the stirrer shaft n.

FIGURE 2. Details of the dissolution ampoule. Stirrer shaft a, inlet tube b, Teflon tubes c, steel tubes d, screw lid e, cylinder f, cylindrical cavity g, scores cut in the cylinder wall h, solid sample i.

FIGURE 3. Recorded power-time curve for dissolution of 8.63 mg acetanilide in water at 298.15 K. The right-hand scale shows the solute molality m as calculated from the derived $\Delta_{\text{sol}}H_m$ (no dynamic correction was applied).

FIGURE 4. The measured enthalpy changes ΔH_{exp} plotted against the number n of moles of acetanilide. ●, 288.01 K; ■, 298.15 K; and ▼, 310.15 K.

FIGURE 5. The measured enthalpy change ΔH_{exp} plotted against the number n of moles of adenine. ●, 288.01 K; ▲, 298.15 K; □, 308.15 K; and ▼, 318.14 K. The line at 288.01 K is not drawn.

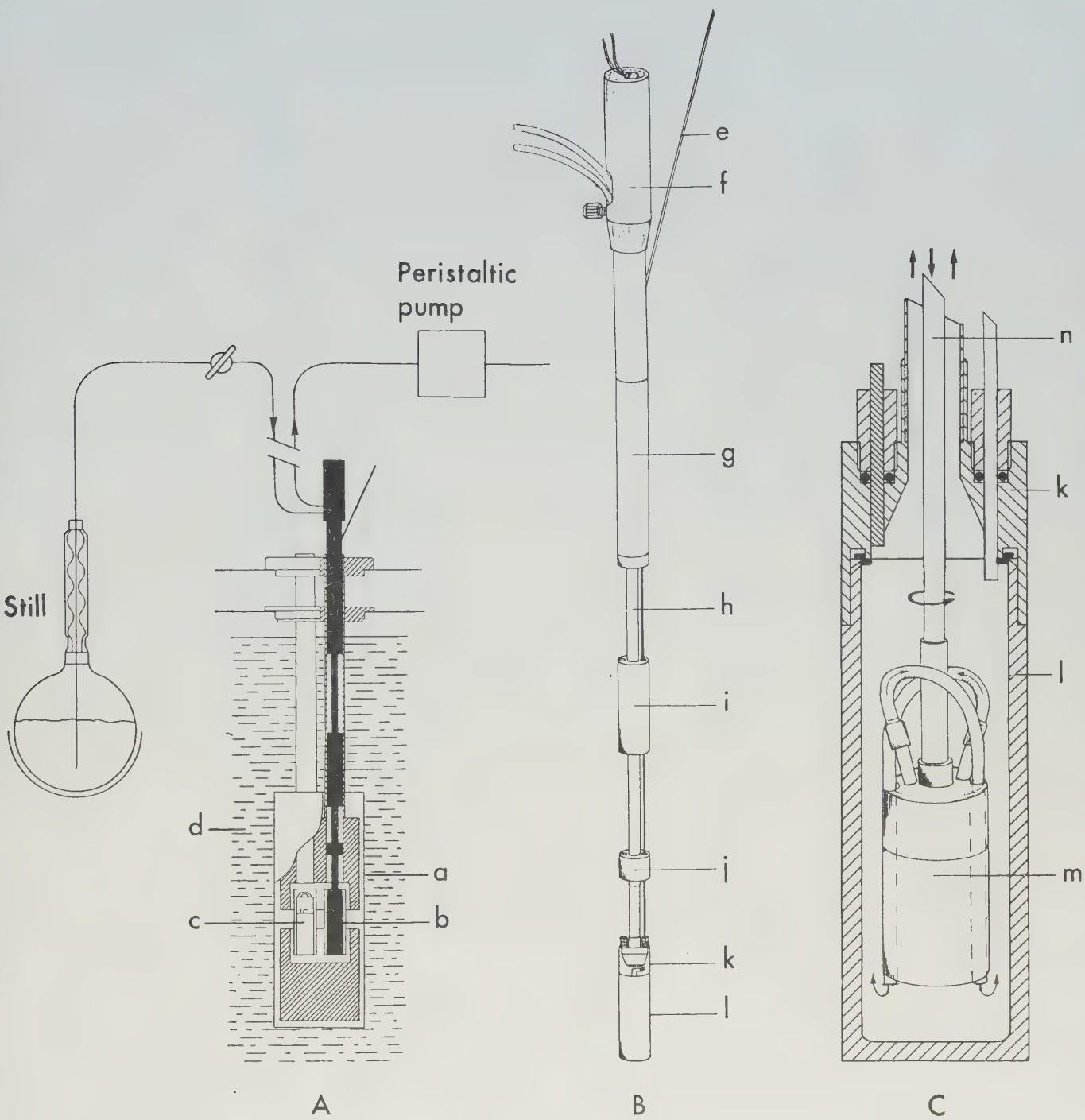


Figure 1

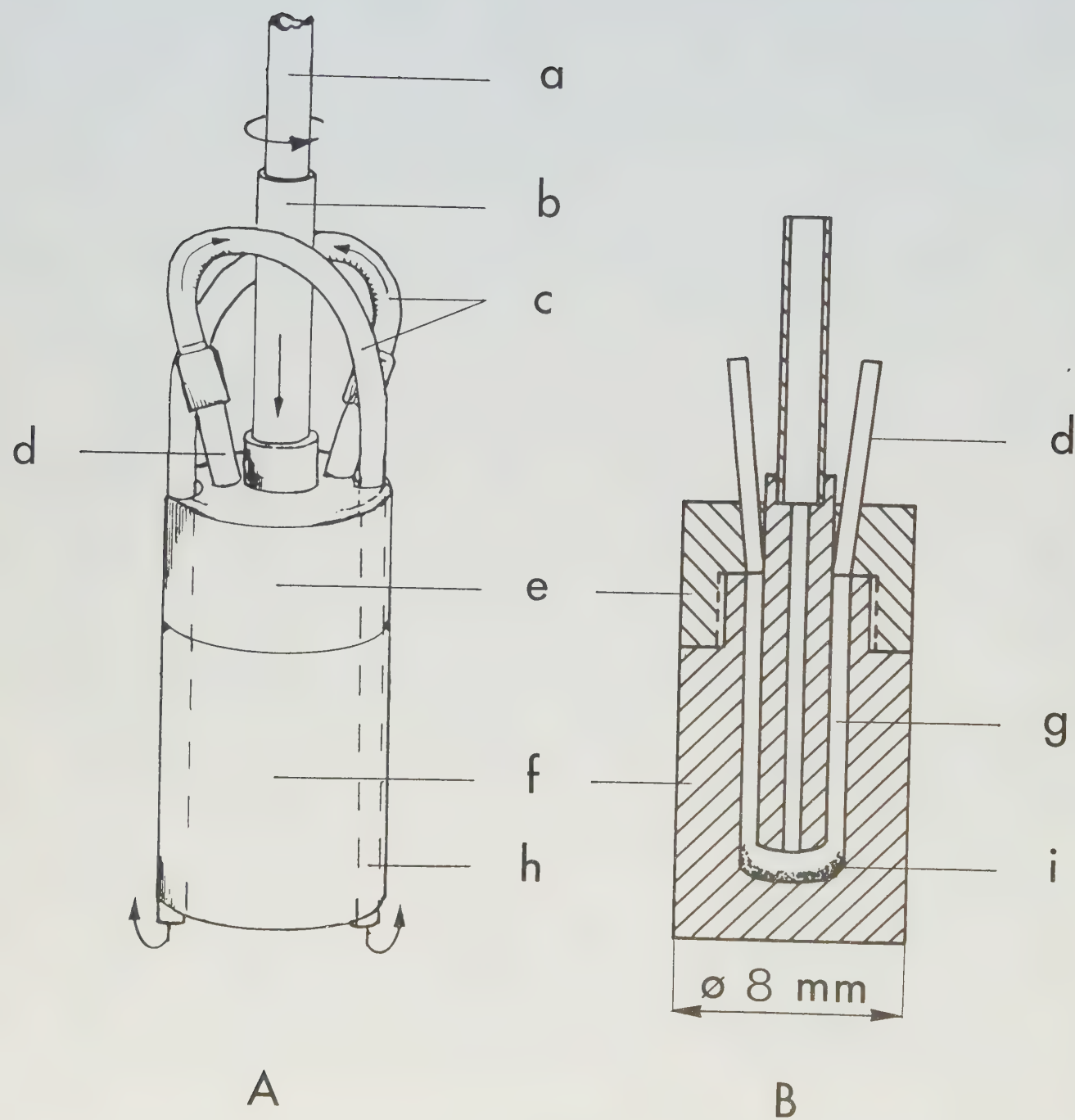


Figure 2

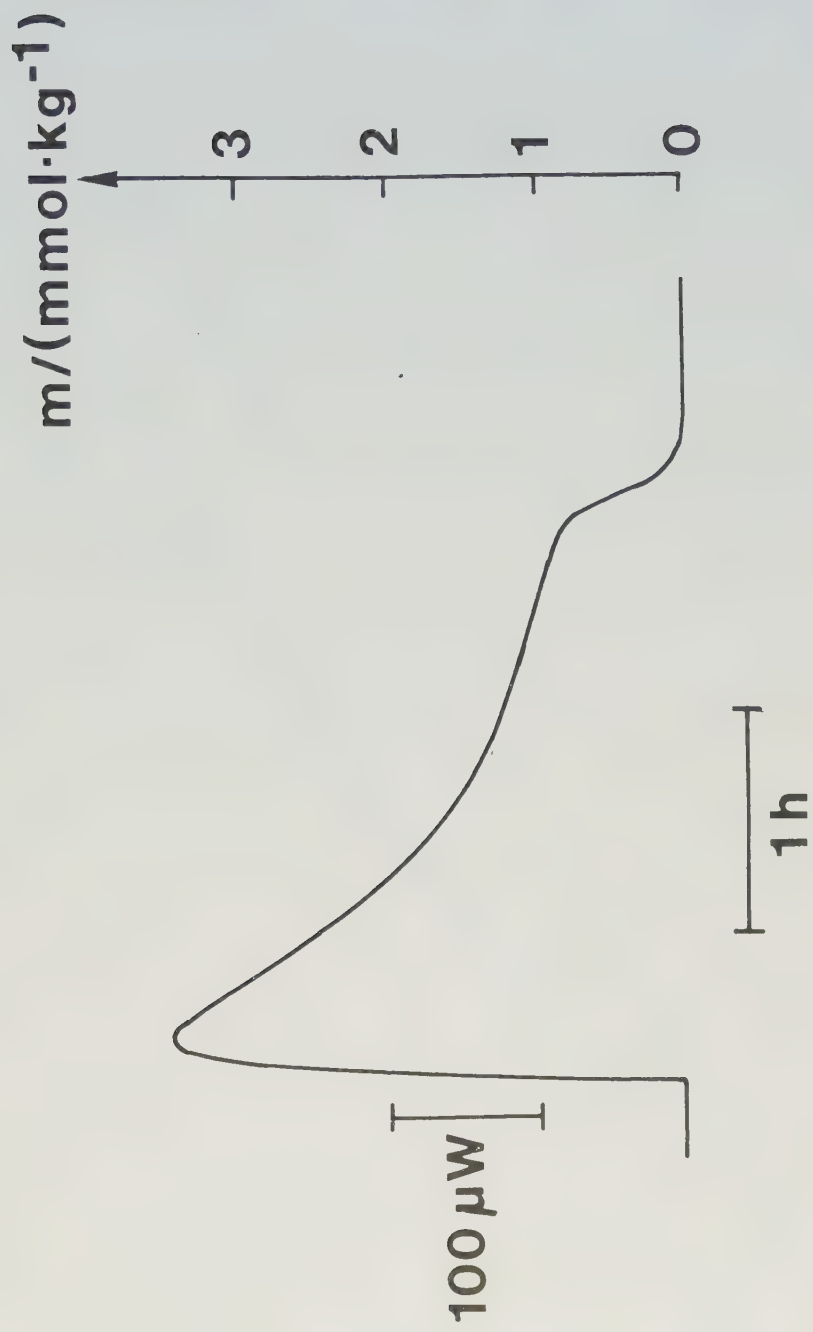


Figure 3

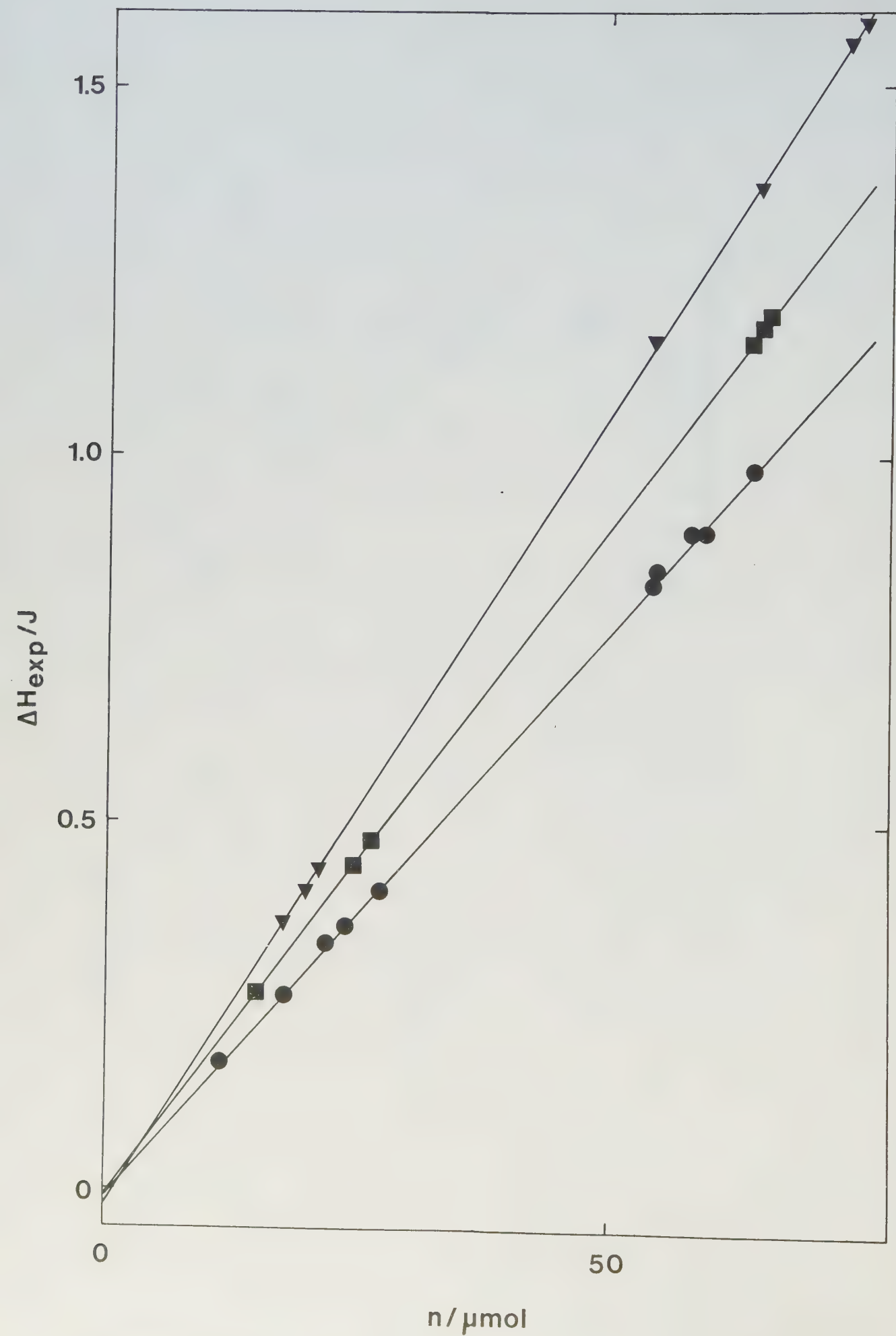


Figure 4

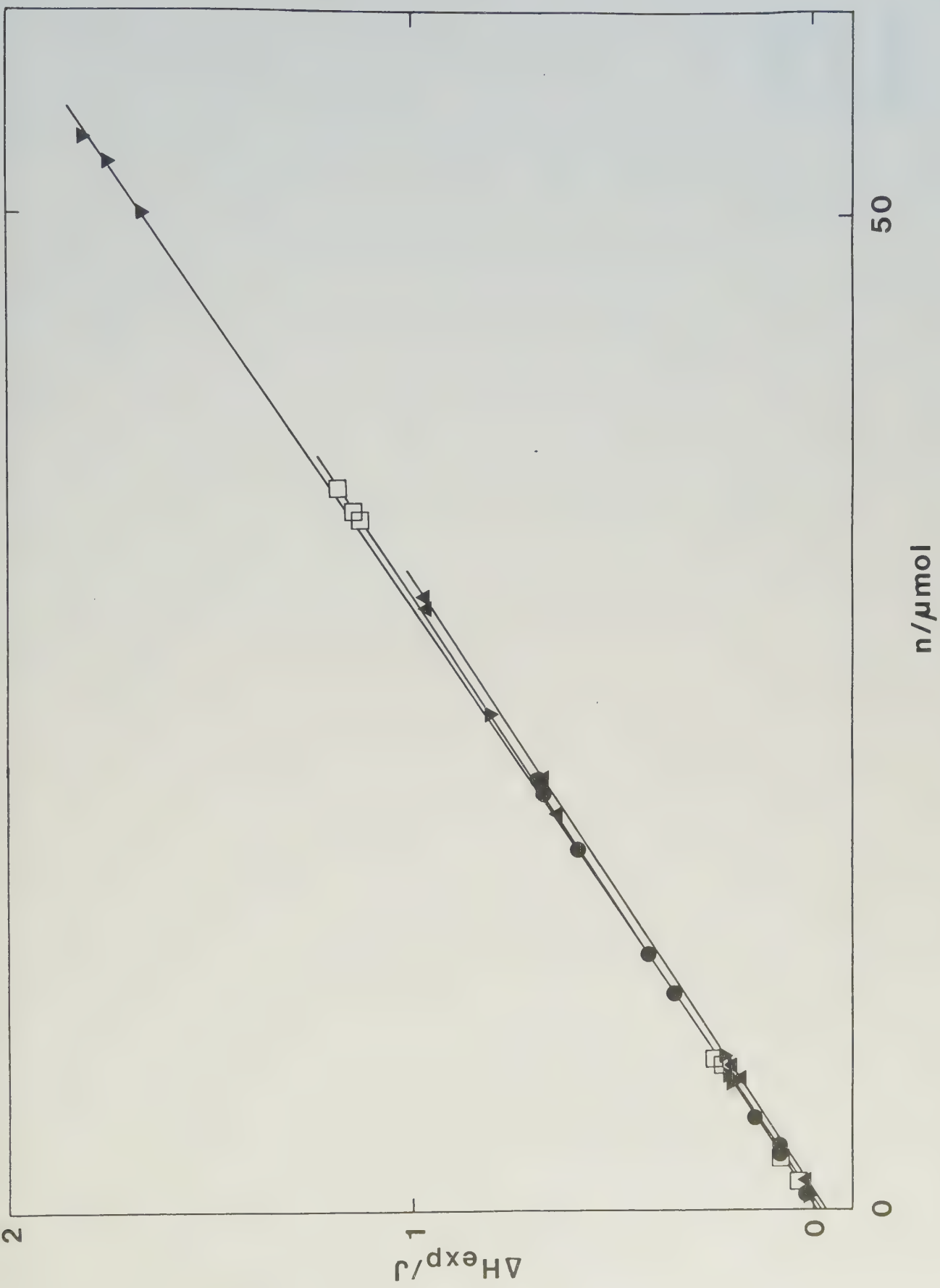


Figure 5

III

ENTHALPIES AND HEAT CAPACITIES FOR N-ALKAN-1-OLS IN H_2O AND D_2O

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ABSTRACT

Enthalpies of dissolution of n-alkan-1-ols in H_2O and in D_2O have been determined calorimetrically at different temperatures. For the $\text{C}_1\text{-C}_4$ compounds, measurements were performed with both H_2O and D_2O as solvents, whereas for $\text{C}_5\text{-C}_8$ only H_2O was used. Results of dilution experiments with the $\text{C}_1\text{-C}_4$ compounds were expressed in terms of second and third virial coefficients. Experiments were performed in the temperature range 284-318 K. Enthalpy and heat capacity values were derived for the infinitely dilute solutions.

INTRODUCTION

The present work is a part of our continuing studies of the thermodynamics of hydrophobic hydration; for previous work in this series see e.g. references 1, 2. Here results of calorimetric measurements of the enthalpies of solution and dilution of n-alkan-1-ols in H_2O and D_2O are reported. The initial part of the work was started several years ago as a joint project with the Department of Chemistry, University of Minnesota (Professor R. Lumry). By use of a precise macrocalorimeter, enthalpies of solution in H_2O and in D_2O were determined over the range of about 284 K to 316 K for the C_1 - C_4 alcohols.⁽³⁾ Following the development of a new microcalorimetric solution technique,⁽⁴⁾ measurements were made for the C_1 - C_8 alcohols in H_2O over a similar temperature range.

A few years ago we developed a new system of microcalorimeters⁽⁵⁾ which includes a flow-mixing calorimeter suitable for precise measurements of enthalpies of dilution. A series of dilution experiments was performed with this instrument for the C_1 - C_4 alcohols in H_2O and in D_2O over the same temperature range as the macrocalorimetric solution experiments.

From the combined results of these different measurements, enthalpies and heat capacities of solution at infinite dilution for C_1 - C_8 in H_2O and C_1 - C_4 in D_2O have been derived.

EXPERIMENTAL

Materials

Methanol, propan-1-ol, and n-butan-1-ol (BDH, Aristos), ethanol (AB Svensk Sprit) n-pentan-1-ol, n-hexan-1-ol, n-heptan-1-ol

and n-octan-1-ol (Fluka puriss) were dried by refluxing over CaH_2 for 3 to 5 h or by sitting over 4A molecular sieves, and were then fractionally distilled. As judged by g.c., purities in all cases were ≥ 99.8 moles per cent. The mass fraction of water, determined by g.c., was ≤ 0.0002 . For the dilution measurements, solutions were prepared from alcohol samples for which the water content was less rigorously controlled. Reagent-grade H_2O produced by a Milli-Q filtration system was used. D_2O was obtained from Norsk Hydro (99.8 moles per cent) and was used as received in the dissolution calorimetric experiments. The D_2O in the solutions obtained from these measurements was contaminated by the hydroxyl hydrogen from the alcohols. The D_2O was recovered by fractional distillation and was used in the flow microcalorimetric dilution experiments. Each batch distilled was analyzed by n.m.r. for its isotopic composition and was found to have ≥ 98.5 moles per cent of D_2O .

Calorimetry

Three different calorimetric techniques were used: enthalpies of solution for the pure alcohols were measured by use of an LKB 8721-1 calorimeter (an isoperibol calorimeter where a sealed sample ampoule is broken in a glass reaction vessel containing 100 cm^3 of solvent), and by use of a microcalorimetric dissolution technique where the sample is injected into a flow of solvent.⁽⁴⁾ Dilution experiments were performed by use of the flow-mixing vessel of the prototype to the LKB BioActivity Monitor (a "4-channel" instrument, where each "channel" is a twin thermopile heat conduction calorimeter).⁽⁵⁾

Dissolution experiments by use of LKB 8721-1. These experiments, which were performed essentially according to our normal procedure, have been described in considerable detail in reference 3. For the D_2O experiments, the charging of the vessel was performed

under a flow of dry N_2 to avoid uptake of H_2O . Filling of the sample ampoules was also performed under the protection of dry N_2 . Analysis for water by g.l.c. on a few randomly selected ampoules showed that the water content of the alcohol samples did not increase significantly during the ampoule filling and sealing procedure.

Particularly for small samples of methanol, a significant part of the substance was in the gaseous state prior to the breaking of the ampoule (volume 1.1 cm^3). From results of separate experiments,⁽³⁾ it was suggested that the sealing techniques used did not give rise to any significant weighing error due to loss of air during the sealing procedure. In calculating the results, it was assumed that the alcohol vapour dissolved quantitatively during the course of the dissolution experiments. A correction was applied for its enthalpy of condensation.

The calorimeter was calibrated electrically before each ampoule breaking and enthalpy values thus refer to the final temperature at the dissolution experiments. Absolute temperature values for all three methods used in this work are believed to be accurate to within $\pm 0.03\text{ K}$.

During the time period for these dissolution experiments, several TRIS-test reactions⁽⁶⁾ were performed. Results were within uncertainty limits identical to the recommended value.⁽⁷⁾

Dissolution experiments using the microcalorimetric injection technique. The instrument and the measurement method have been described in detail.⁽⁴⁾ A constant flow of H_2O (about $10\text{ mm}^3\cdot\text{s}^{-1}$) was sucked through the channel system of the calorimetric vessel. Solute

was introduced into the dissolution zone by use of a thin steel tube (i.d. 0.15 mm) attached to a modified⁽⁴⁾ 100 mm³ gastight Hamilton syringe positioned in a motor-driven syringe drive. Typically about 5 mm³ of alcohol was injected during 30 min.

For n-octan-1-ol a modified version of the injection vessel described in reference 4 was used together with a regular twin calorimeter of the LKB BioActivity Monitor.⁽⁵⁾ The latter instrument has a thermostatic bath that is 10 times more stable than that used with the original vessel. Necessary integration times varied with the measurement temperature and the solute. For instance, at 298.15 K the integration time for methanol was 1 h, whereas about 8 h were needed for n-octan-1-ol. Preliminary experiments with the latter substance, carried out with the original vessel⁽⁴⁾ and its moderately stable thermostatic bath, gave about 6 times lower precision than those which will be reported here.

For the most volatile and most easily diffusible compounds, small corrections were applied for diffusion through the tip of the injection tube and possible leakage through the seal between the plunger and the barrel of the syringe. Corrections were not significant for n-hexan-1-ol and the higher alcohols.

Electrical calibrations could be determined automatically in connection with each series of measurements. This was valuable, as the calibration value was quite sensitive to changes in the solvent flow rate, about 0.4 per cent for a flow-rate variation of 1 mm³·s⁻¹. However, we have found that electrical calibrations with the present type of calorimetric vessels can easily be impaired by significant systematic errors, as the position and/or design of the heater is very critical. We therefore use a suitable test reaction in order to

correct empirically the electrical calibration values.⁽⁴⁾ In the present case we have used the dissolution of propan-1-ol at 298.15 K; for which accurate values were determined by the microcalorimetric method. Corrections amounted to 0.3 per cent.

Dilution experiments. The flow-mixing vessel, the calorimeter and the working procedure were described in reference 5. HPLC pumps (LKB 2210) were used to pump the alcohol solution and the solvent. For each compound, three or four solutions with different molalities of alcohol were mixed with the solvent. For each solution, four different flow-rate combinations (solution + solvent) were used, but the sum of the flow rates was in all cases $0.7 \text{ cm}^3 \cdot \text{s}^{-1}$.

Molalities of the starting solutions and of the flow rates were determined by weighing. The instrument was calibrated electrically.⁽⁵⁾

RESULTS AND DISCUSSION

Dilution experiments.

Results of flow microcalorimetric dilution experiments for the C_1 - C_4 alcohols were expressed in terms of the virial coefficients expansion according to the McMillan-Mayer theory,^(8, 9) eqn (1).

$$H_m^E(m) = h_{xx}m + h_{xxx}m^2 + \dots, \quad (1)$$

where $H_m^E(m)$ is the molar excess enthalpy for a solution of a solute of molality m . The molar enthalpy of dilution, $\Delta_{dil}H_m$, is identical to the change in the excess enthalpy following a dilution process where the molality will change from m_i to m_f

$$\Delta_{dil} H_m(m_i \rightarrow m_f) = H_m^E(m_f) - H_m^E(m_i) = h_{xx}(m_f - m_i) + h_{xxx}(m_f^2 - m_i^2) + \dots \quad (2)$$

In the present case solute molalities were low and virial coefficients higher than h_{xxx} were found to be negligible. Eqn. (2) then takes the form

$$\frac{\Delta_{dil} H_m(m_i \rightarrow m_f)}{m_f - m_i} = h_{xx} + h_{xxx}(m_f + m_i) \quad (3)$$

From the linear expression (3), h_{xx} and h_{xxx} were derived as the intercept and the slope, respectively. Results are summarized in tables 1 and 2. Uncertainties are twice the standard deviation.

In tables 1 and 2, literature values are also given for the studied alcohols in H_2O at 298.15 K. Except for propan-1-ol in H_2O at 278.15 K,⁽¹⁰⁾ no values for the virial coefficients at other temperatures, or in D_2O , seem to have been determined. For methanol, ethanol and propan-1-ol, there is good agreement with literature values. For n-butan-1-ol, a rather wide range of values has been reported, which might be due to the choice of molality ranges. However, the present values are in good agreement with those reported by Perron and Desnoyers.⁽¹³⁾

Inspection of the tables shows that there is an increase in both h_{xx} and h_{xxx} with the length of the alkyl chain, with the notable exception of the h_{xxx} value for n-butan-1-ol in D_2O at the lowest temperature.

Franks et al⁽⁹⁾ have discussed the cooperativity of hydrophobic

interaction by comparing the contributions of pair and triplet effects at a given molality as a function of the number of carbon atoms, N_C . As an example, they have compared the ratio h_{xxx}/h_{xx} at molalities of $1 \text{ mol} \cdot \text{kg}^{-1}$ for ethanol and n-butan-1-ol at 298.15 K, obtaining 0.27 and 0.64, respectively. However, in a later article,⁽¹⁰⁾ Franks and Pedley discussed the risk of interpreting enthalpies in terms of molecular interactions at a single temperature. This is well-illustrated by the values shown in tables 1 and 2. An extreme example is given by n-butan-1-ol in D_2O , for which the ratio h_{xxx}/h_{xx} varies from -0.11 at 283.85 K to 0.32 at 315.63 K.

From the variation of h_{xx} and h_{xxx} with temperature, corresponding second and third virial coefficients of the heat capacity can be obtained, $c_{xx} = \frac{dh_{xx}}{dT}$ and $c_{xxx} = \frac{dh_{xxx}}{dT}$, respectively. Figures 1 and 2 show plots of h_{xx} and h_{xxx} versus T . The temperature dependences of h_{xx} are seen to be more pronounced for D_2O as solvent. The c_{xx} -values have been estimated by a semi-graphical method⁽¹⁴⁾ with the assumption that c_{xx} varies linearly with temperature. The c_{xx} values are shown in table 3. Uncertainties were estimated graphically.

The c_{xx} obtained for the alcohols in H_2O are very close to zero but with a weak tendency to become more positive with increasing alkyl chain length. Furthermore, there are no significant differences between ethanol, propan-1-ol and n-butan-1-ol. In D_2O , all the c_{xx} values are significantly below zero and all are close to $-5 \text{ J} \cdot \text{kg} \cdot \text{K}^{-1} \cdot \text{mol}^{-2}$.

We do not believe that our experimental results will lead to very accurate values of c_{xxx} . However, if the temperature dependence of h_{xxx} is treated in the same way as was done for h_{xx} , the following c_{xxx} values, with H_2O as solvent, can be estimated: methanol ($0.0 \pm$

0.5); ethanol (1.1 ± 1.0); propan-1-ol (2.0 ± 2.5) and n-butan-1-ol (8.2 ± 3.1) $\text{J}\cdot\text{kg}^2\cdot\text{K}^{-1}\cdot\text{mol}^{-3}$.

In table 3 are also shown literature values of c_{xx} with H_2O as solvent. They agree well with our results for methanol and ethanol, but not for propan-1-ol and n-butan-1-ol. The values reported in references 13 and 15 were derived from results of direct heat capacity measurements of dilute alcohol solutions, m_{max} being about $1 \text{ mol}\cdot\text{kg}^{-1}$. Jolicoeur and Lacroix⁽¹⁵⁾ did not take contributions from c_{xxx} into account. These were also disregarded by Perron and Desnoyers.⁽¹³⁾

The following discussion suggests that neglect of c_{xxx} contributions can lead to the differences observed. Molar excess heat capacities, $C_{p,m}^E$ can be calculated by:

$$C_{p,m}^E(m) = c_{xx}m + c_{xxx}m^2 + \dots \quad (4)$$

It is seen that if c_{xxx} contributions are neglected, $C_{p,m}^E$ values for $1 \text{ mol}\cdot\text{kg}^{-1}$ solutions are numerically identical to the corresponding c_{xx} values. With our values for c_{xx} and c_{xxx} (and disregarding higher terms) we obtain for $1 \text{ mol}\cdot\text{kg}^{-1}$ solutions of propan-1-ol and n-butan-1-ol $C_{p,m}^E = (3.3 \pm 2.9)$ and $(9.5 \pm 3.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively. These values are close to the literature values for c_{xx} shown in table 3.

Solution experiments

Results of the macrocalorimetric solutions experiments in H_2O and D_2O are summarized in table 4. Within each series, molalities for the solutes (m) normally varied between 0.01 and $0.06 \text{ mol}\cdot\text{kg}^{-1}$.

Within uncertainty limits, a linear dependence was found for

$\Delta_{\text{sol}}H_m$ with m which could be used for extrapolation to the enthalpy value at infinite dilution, $\Delta_{\text{sol}}H_m^\infty$.⁽³⁾ However, considerably more precise extrapolations can be made by use of eqn. (3) and the results from the microcalorimetric solution experiments. Molar enthalpies of dilution to infinite dilution ($m_f = 0$) are given by

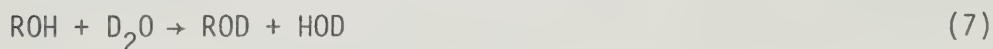
$$\Delta_{\text{dil}}H_m^\infty = -h_{xx}m - h_{xxx}m^2 \quad (5)$$

For the present values for m , the h_{xxx} term is not significant and thus

$$\Delta_{\text{sol}}H_m^\infty = \Delta_{\text{sol}}H_m - h_{xx}m \quad (6)$$

Corrections to infinite dilution, which increase with the length of the alkyl chain, are in all cases $< 0.10 \text{ kJ}\cdot\text{mol}^{-1}$.

For the experiments conducted in D_2O , the $\Delta_{\text{sol}}H_m^\infty$ values include enthalpy changes for the isotopic exchange reaction



The derived $\Delta_{\text{sol}}H_m^\infty$ values were fitted to a quadratic equation

$$\Delta_{\text{sol}}H_m^\infty(T) = a + bT + cT^2, \quad (8)$$

for which the values for the constants are given in table 5. Values for the C_5 - C_8 alcohols, determined by use of microcalorimetric injection technique (see table 6), are also given in table 5.

Table 6 summarizes the results of the microcalorimetric dissolution measurements which were performed at 288.15 K, 298.15 K,

308.15 K and 318.15 K for the C_1 - C_8 alcohols in H_2O (column A).

Uncertainties are twice the overall standard deviation of the mean.

For each compound and temperature, 8 to 10 measurements were usually made. The final concentration was low in all cases: for methanol $0.006 \text{ mol} \cdot \text{dm}^{-3}$, for ethanol $0.004 \text{ mol} \cdot \text{dm}^{-3}$, and for the other solutes, $< 0.003 \text{ mol} \cdot \text{dm}^{-3}$. In all cases, the final concentrations were judged to be low enough to ignore the enthalpies of dilution so that the experimental solution enthalpies were taken as identical to $\Delta_{\text{sol}} H_m^\infty$.

In table 6, $\Delta_{\text{sol}} H_m^\infty$ values for the C_1 - C_4 alcohols derived from values in tables 4 and 5 are also shown (column B). The two sets of results are in all cases in full agreement but the values based on the macrocalorimetric dissolution experiments are more precise and are considered as our best values, cf. table 7.

Some macrocalorimetric dissolution measurements were also made for n-pentan-1-ol in H_2O at 298.43 K. Extrapolation to infinite dilution led to $\Delta_{\text{sol}} H_m = -(7.84 \pm 0.08) \text{ kJ} \cdot \text{mol}^{-1}$; correction to 298.15 K gave $\Delta_{\text{sol}} H_m^\infty = -(7.93 \pm 0.08) \text{ kJ} \cdot \text{mol}^{-1}$, in full agreement with the microcalorimetric value given in table 6. For n-hexan-1-ol and the higher alcohols, the present macrocalorimetric method could not be used for accurate work.

In figure 3, $\Delta_{\text{sol}} H_m^\infty$ values are plotted versus the number of carbon atoms, N_C , at 288.15 K, 298.15 K, 308.15 K and 318.15 K. It is seen that at each temperature a linear relation is obtained for $N_C \geq 5$. These values are accurately summarized by the equation

$$\Delta_{\text{sol}} H_m^{\infty} / (\text{kJ} \cdot \text{mol}^{-1}) = -146.272 + 0.79482T/\text{K} - 1.19503 \cdot 10^{-3} T^2/\text{K}^2 + (0.04893T/\text{K} - 13.07)N_c \quad (9)$$

The mean deviations between experimental and calculated $\Delta_{\text{sol}} H_m^{\infty}$ values are $0.04 \text{ kJ} \cdot \text{mol}^{-1}$ at 288.15 K, $0.03 \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K, $0.05 \text{ kJ} \cdot \text{mol}^{-1}$ at 308.15 K and $0.09 \text{ kJ} \cdot \text{mol}^{-1}$ at 318.15 K. The experimental value for n-heptan-1-ol at 318.15 K appears to be slightly in error, as it is as much as $0.17 \text{ kJ} \cdot \text{mol}^{-1}$ lower than the calculated value, cf. table 5, where the constants for n-heptan-1-ol deviates from the trend.

In table 7, $\Delta_{\text{sol}} H_m^{\infty}$ values at 298.15 K obtained in this work are compared with values from earlier work. For the dissolution of the C_1 - C_4 alcohols in H_2O , Abraham⁽¹⁶⁾ has recently derived mean values which in all cases are in excellent agreement with the present results. For the higher alcohols, the agreement is in several cases less satisfactory. This also applies to the values for D_2O .

Solvation enthalpies, i.e. enthalpy changes for the transfer of the molecules from the ideal gas to infinitely dilute solution, $\Delta_{\text{sol}} H_m^{\infty}$, were calculated from:

$$\Delta_{\text{sol}} H_m^{\infty} = \Delta_{\text{sol}} H_m^{\infty} - \Delta_{\text{vap}} H_m^0, \quad (10)$$

where $\Delta_{\text{vap}} H_m^0$ is the enthalpy of vaporization to form the ideal gas. Values for $\Delta_{\text{sol}} H_m^{\infty}$ at 298.15 K are given in table 8 and in figure 4. The used $\Delta_{\text{vap}} H_m^0$ values are also given in table 8.

For D_2O as solvent, the $\Delta_{\text{sol}} H_m^{\infty}$ values have been corrected for the isotope exchange reaction (7) in order to make them more directly comparable with the corresponding values for H_2O . The

correction term has been determined by Chand and Fenby ⁽²⁷⁾ for methanol and ethanol to be $\Delta H_m = -(0.32 \pm 0.01) \text{ kJ}\cdot\text{mol}^{-1}$. This value was also used for propan-1-ol and n-butan-1-ol.

The $\Delta_{\text{sol}} H_m^\infty$ are slightly more negative for D_2O than for H_2O , the differences increasing with increasing chain length. From figure 4 it is seen that $-\Delta_{\text{sol}} H_m^\infty$ increases linearly with increasing chain length after C_3 . This agrees with Abraham's conclusion based on earlier work. ⁽¹⁶⁾ The slope of the line, i.e. the transfer enthalpy for $-\text{CH}_2-$ from the gas phase to infinitely dilute solution, is $-3.2 \text{ kJ}\cdot\text{mol}^{-1}$ for $N_C \geq 4$, slightly less exothermic than the value given by Abraham, ⁽¹⁶⁾ $-3.56 \text{ kJ}\cdot\text{mol}^{-1}$.

Heat capacity values

Differentiation of eqn. (8) with respect to T gives the change in heat capacity, $\Delta_{\text{sol}} C_{p,m}^\infty$. The values are listed in tables 9 and 10 for H_2O and D_2O , respectively. In the tables are also given the partial molar heat capacities at infinite dilution, $C_{p,2}^\infty$, which were calculated from the equation

$$C_{p,2}^\infty = \Delta_{\text{sol}} C_{p,m}^\infty + C_{p,m}^*, \quad (11)$$

where $C_{p,m}^*$ is the molar heat capacity of the pure solute.

Uncertainties given in tables 9 and 10 are twice the overall standard deviation of the mean. The uncertainties for $\Delta_{\text{sol}} C_{p,m}^\infty$ were calculated by a semigraphical method. ⁽¹⁴⁾

In table 9 are also shown $C_{p,2}^\infty$ values calculated by an empirical group additivity scheme developed some years ago, ⁽²⁸⁾ $C_{p,2}^\infty(\text{calc})$.

With the exception of the value for methanol, the differences between

experimental and calculated values are small, further confirming the exceptional additivity for group values of $C_{p,2}^{\infty}$ for nonionic compounds in aqueous solutions. The CH_2 -increment for aqueous solutions is $90 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, which is identical to the mean value from several groups of compounds reported earlier.⁽²⁸⁾ For D_2O solutions, the CH_2 -increments appear to be slightly higher, 112, 97 and $93 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for the values given in table 10, but the series is too short to draw any definite conclusions. A plot of $C_{p,2}^{\infty}$ values versus the number of carbon atoms is shown in figure 5.

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REFERENCES

1. Lian, Y.-N.; Chen, A.-T.; Suurkuusk, J.; Wadsö, I. *Acta Chem. Scand.* 1982, A36, 735.
2. Olofsson, G.; Oshodi, A. A.; Qvarnström, E.; Wadsö, I. *J. Chem. Thermodynamics* 1984, 16, 1041.
3. Rothschild, W. Ph. D. thesis, 1981. University of Minnesota.
4. Nilsson, S.-O.; Wadsö, I. *J. Chem. Thermodynamics* 1984, 16, 317.
5. Suurkuusk, J.; Wadsö, I. *Chemica Scripta* 1982, 20, 155.
6. Hill, J. O.; Öjelund, G.; Wadsö, I. *J. Chem. Thermodynamics* 1969, 1, 111.
7. Prosen, E. J.; Kilday, M. V. *J. Res. Nat. Bur. Stand.* 1973, 77A, 581.
8. McMillan, M.; Mayer, J. *J. Chem. Phys.* 1945, 13, 276.
9. Franks, F.; Pedley, M. D.; Reid, M. D. *J. Chem. Soc. Faraday Trans. I*, 1976, 72, 359.
10. Franks, F.; Pedley, M. D. *J. Chem. Soc. Faraday Trans. I*, 1983, 79, 2249.
11. Dimmling, W.; Lange, E.; *Z. Elektrochem.* 1951, 55, 322.
12. Lange, E.; Möhring, K. *Z. Elektrochem.* 1953, 57, 660.
13. Perron, G.; Desnoyers, J. E. *J. Chem. Thermodynamics* 1981, 13, 1105.
14. Lark, P. D.; Craven, B. R.; Bosworth, R. C. L. *The handling of chemical data.* Pergamon Press: Oxford. 1968.
15. Jolicoeur, C.; Lacroix, G. *Can. J. Chem.* 1976, 54, 624.
16. Abraham, M. H. *J. Chem. Soc., Faraday Trans. I*, 1984, 80, 153.
17. Aveyard, R.; Mitchell, D. L. *Trans. Faraday Soc.* 1968, 64, 1757.
18. Rouw, H. C.; Somsen, G. *J. Chem. Thermodynamics* 1981, 13, 67.
19. Bury, R.; Treiner, C. *J. of Coll. and Interface Sci.* 1985, 103, 1.
20. Arnett, E. M.; Kover, W. B.; Carter, J. V. *J. Am. Chem. Soc.* 1969,

91, 4028.

21. Hill, D. J. T.; White, L. R. Aust. J. Chem. 1974, 27, 1905.
22. Arnett, E. M.; McKelvey, M. R. in "Solute-Solvent Interactions", Coetzer, J. F.; Ritchie, C. D. (eds), Marcel Dekker, New York, Chapter 6 (1969).
23. Krishnan, C. V.; Friedman, H. L. J. Phys. Chem. 1969, 73, 1572.
24. Hill, D. J. T.; Malar, C. Aust. J. Chem. 1975, 27, 6.
25. Mayer, V.; Svoboda, V.; Uchytlova, V.; Finke, M. Fluid Phase Equilibria 1985, 20, 111.
26. Månsson, M.; Sellers, P.; Stridh, G.; Sunner, S. J. Chem. Thermodynamics 1977, 9, 91.
27. Chand, A.; Fenby, D. V. J. Chem. Thermodynamics 1978, 10, 997.
28. Nichols, N.; Sköld, R.; Spink, C.; Suurkuusk, J.; Wadsö, I. J. Chem. Thermodynamics 1976, 8, 1081.

TABLE 1. Second virial coefficients of enthalpy, h_{xx} , for n-alkan-1-ols in H_2O and in D_2O at 283.85 K, 298.15 K and 315.63 K.

Solute	Solvent	Molality ranges/(mol·kg ⁻¹)		$h_{xx}/(J·kg·mol^{-2})$		
		Initial	Final	283.85 K	298.15 K	315.63 K
CH ₃ OH	H ₂ O	0.19-0.80	0.02-0.60	275 ± 2	224 ± 3 (246 ^a , 218 ^b)	178 ± 11
	D ₂ O	0.23-1.03	0.06-0.67	411 ± 3	314 ± 5	252 ± 3
C ₂ H ₅ OH	H ₂ O	0.11-0.70	0.03-0.45	270 ± 5	250 ± 4 (230 ^a , 248 ^{lb} , 243 ^c)	271 ± 7
	D ₂ O	0.22-0.60	0.04-0.38	498 ± 7	385 ± 7	344 ± 10
C ₃ H ₇ OH	H ₂ O	0.15-0.55	0.03-0.36	550 ± 7	557 ± 12 (477 ^a m 540 ^b , 559 ^c)	591 ± 11
	D ₂ O	0.10-0.54	0.01-0.35	906 ± 19	794 ± 11	776 ± 16
C ₄ H ₉ OH	H ₂ O	0.07-0.46	0.01-0.26	1226 ± 15	1245 ± 11 (1225 ^b , 1003 ^c , 1170 ^d)	1265 ± 14
	D ₂ O	0.11-0.30	0.01-0.19	1858 ± 13	1680 ± 23	1672 ± 27

^a Ref. 11

^b Ref. 13

^c Ref. 9

^d Ref. 12

TABLE 2. Third virial coefficients of enthalpy, h_{xxx} , for n-alkan-1-ols in H_2O and in D_2O at 283.35 K, 298.15 K and 315.63 K. Molality ranges see table 1.

Solute	Solvent	$h_{xxx}/(J \cdot kg^2 \cdot mol^{-3})$		
		283.85 K	298.15 K	315.63 K
CH_3OH	H_2O	13 ± 3	16 ± 4 (12^a)	11 ± 3
	D_2O	-6 ± 2	11 ± 6	5 ± 6
C_2H_5OH	H_2O	86 ± 7	77 ± 7 (76^a ; 66^b)	47 ± 9
	D_2O	36 ± 10	80 ± 12	110 ± 23
C_3H_7OH	H_2O	156 ± 11	178 ± 22 (213^a ; 158^b)	223 ± 23
	D_2O	65 ± 31	174 ± 22	225 ± 36
C_4H_9OH	H_2O	279 ± 27	460 ± 23 (516^a ; 646^b)	505 ± 22
	D_2O	-201 ± 40	297 ± 78	537 ± 100

^a Ref. 13

^b Ref. 9

TABLE 3. Estimated second virial coefficients of heat capacity, c_{xx} ,
for n-alkan-1-ols in H_2O and in D_2O at 298.15 K.

Solute	$c_{xx}/(J \cdot kg \cdot K^{-1} \cdot mol^{-2})$	
	H_2O	D_2O
CH_3OH	-3.2 ± 1.0 (-3.2^a ; -4.7^b)	-5.3 ± 0.5
C_2H_5OH	-0.5 ± 1.1 (-0.7^a ; -0.6^b)	-5.4 ± 1.0
C_3H_7OH	1.1 ± 1.4 (6.0^a ; 3.8^b)	-4.8 ± 1.3
C_4H_9OH	1.3 ± 1.6 (13.7^a ; 15.6^b)	-5.9 ± 2.5

^a Ref. 13

^b Ref. 15

TABLE 4. Enthalpies of solution at infinite dilution of some n-alkan-1-ols in H₂O or D₂O determined by use of the LKB 8721-1 instrument. N is the number of experiments. Uncertainties are twice the overall standard deviation of the mean.

Solute	H ₂ O			D ₂ O ^a		
	T/K	N	$\Delta_{\text{sol}}H_m^\infty/(\text{kJ}\cdot\text{mol}^{-1})$	T/K	N	$\Delta_{\text{sol}}H_m^\infty/(\text{kJ}\cdot\text{mol}^{-1})$
CH ₃ OH	283.87	5	-8.43 $\pm$ 0.02	283.85	5	- 9.44 $\pm$ 0.02
	298.46	8	- 7.28 $\pm$ 0.01	298.51	5	- 8.17 $\pm$ 0.02
	315.60	7	- 6.03 $\pm$ 0.02	315.61	4	- 6.79 $\pm$ 0.03
C ₂ H ₅ OH	283.87	5	-12.36 $\pm$ 0.03	283.85	4	-13.89 $\pm$ 0.03
	298.43	6	-10.12 $\pm$ 0.01	298.46	4	-11.37 $\pm$ 0.02
	315.51	6	- 7.68 $\pm$ 0.02	315.61	4	- 8.70 $\pm$ 0.02
C ₃ H ₇ OH	283.88	5	-13.27 $\pm$ 0.02	283.85	5	-15.10 $\pm$ 0.02
	298.44	6	-10.10 $\pm$ 0.02	298.46	5	-11.55 $\pm$ 0.02
	315.60	7	- 6.69 $\pm$ 0.03	315.61	4	- 7.78 $\pm$ 0.02
C ₄ H ₉ OH	283.86	6	-13.20 $\pm$ 0.02	283.85	4	-15.18 $\pm$ 0.03
	298.43	6	- 9.20 $\pm$ 0.02	298.44	4	-10.78 $\pm$ 0.05
	315.61	4	- 4.88 $\pm$ 0.03	315.61	4	- 6.06 $\pm$ 0.04

^a $\Delta_{\text{sol}}H_m^\infty$ values include contributions for the isotopic exchange reaction.

TABLE 5. Values for coefficients in eqn. (8) calculated from data in table 4 (C_1 - C_4 compounds) and in table 6, columns (A) (C_5 - C_8 compounds).

Solute	Sol-vent	$a/(\text{kJ}\cdot\text{mol}^{-1})$	$b/(\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	$10^4 \cdot c/(\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-2})$
CH_3OH	H_2O	- 45.591	0.18068	-1.7529
	D_2O	- 49.847	0.19534	-1.8666
$\text{C}_2\text{H}_5\text{OH}$	H_2O	- 86.480	0.36288	-3.5852
	D_2O	-107.661	0.48050	-5.2895
$\text{C}_3\text{H}_7\text{OH}$	H_2O	-123.748	0.55276	-5.7623
	D_2O	-145.847	0.66760	-7.2919
$\text{C}_4\text{H}_9\text{OH}$	H_2O	-152.825	0.69856	-7.2813
	D_2O	-171.941	0.79070	-8.4000
$\text{C}_5\text{H}_{11}\text{OH}$	H_2O	-184.74	0.86162	-9.0154
$\text{C}_6\text{H}_{13}\text{OH}$	H_2O	-206.61	0.96786	-9.9389
$\text{C}_7\text{H}_{15}\text{OH}$	H_2O	-285.26	1.45442	-17.2433
$\text{C}_8\text{H}_{17}\text{OH}$	H_2O	-249.58	1.17612	-11.7503

TABLE 6 (cont.)

$C_7H_{15}OH$	H_2O	-9.35 ± 0.08	-4.88 ± 0.07	-0.84 ± 0.05	2.94 ± 0.07
$C_8H_{17}OH^b$	H_2O	-8.24 ± 0.10	-3.37 ± 0.09	1.27 ± 0.05	5.67 ± 0.09

a. Reference value, cf. the text.

b. A modified vessel was used, cf. the text.

TABLE 7. Enthalpies of solution at infinite dilution for some n-alkan-1-ols in H₂O or D₂O at 298.15 K. A comparison between values in this work and values in literature.

Solute	$\Delta_{\text{sol}} H_{\text{m}}^{\infty} / (\text{kJ} \cdot \text{mol}^{-1})$			
	H ₂ O		D ₂ O ^a	
	This work ^b	Literature ^c	This work ^b	Literature ^c
CH ₃ OH	-7.30 $\pm$ 0.01	-7.28 ^e	-8.20 $\pm$ 0.02	-8.24 $\pm$ 0.38 ^l -8.03 ^m
C ₂ H ₅ OH	-10.16 $\pm$ 0.01	-10.17 ^e	-11.42 $\pm$ 0.02	-11.63 $\pm$ 0.13 ^l -11.38 ^m -11.20 $\pm$ 0.08 ⁿ
C ₃ H ₇ OH	-10.16 $\pm$ 0.02	-10.13 ^e	-11.62 $\pm$ 0.02	-11.72 ^m -11.40 $\pm$ 0.08 ⁿ
C ₄ H ₉ OH	-9.27 $\pm$ 0.02	-9.29 ^e	-10.86 $\pm$ 0.05	-11.05 ^m -10.62 $\pm$ 0.08 ⁿ -10.29 $\pm$ 0.09 ^l
C ₅ H ₁₁ OH	-7.99 $\pm$ 0.06	-8.08 $\pm$ 0.42 ^f -7.72 $\pm$ 0.03 ^g -6.65 ^h -7.82 $\pm$ 0.05 ⁱ		
C ₆ H ₁₃ OH	-6.41 $\pm$ 0.04	-6.50 $\pm$ 0.13 ^j -5.77 $\pm$ 0.42 ^f -4.94 ^h		
C ₇ H ₁₅ OH	-4.88 $\pm$ 0.07	-5.30 $\pm$ 0.15 ^j -3.00 ^h		
C ₈ H ₁₇ OH	-3.37 $\pm$ 0.09	-0.05 ^h -3.2 ^k		

- a The enthalpy values include the isotopic exchange reaction.
- b Uncertainties are twice the overall standard deviation of the mean.
- c For uncertainties assigned see references
- d Enthalpy value from measurement with the LKB 8721-1 instrument, see the text.
- e Ref. 16
- f Ref. 17
- g Ref. 18
- h Ref. 19
- i Ref. 20
- j Ref. 21
- k Ref. 21, extrapolated from experimental values.
- l Ref. 22
- m Ref. 23
- n Ref. 24

TABLE 8. Enthalpies of vaporization and solvation at infinite dilution for some n-alkan-1-ols in H₂O or D₂O at 298.15 K. The uncertainties are estimates for C₁-C₆ alcohols and twice the overall standard deviation of the mean, for C₇-C₈ alcohols.

Solute	$\Delta_{\text{vap}} H_m^0 / (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{\text{solv}} H_m^\infty / (\text{kJ} \cdot \text{mol}^{-1})$	
		H ₂ O	D ₂ O ^a
CH ₃ OH	37.83 $\pm$ 0.23 ^b	-45.13 $\pm$ 0.23	-45.71 $\pm$ 0.23
C ₂ H ₅ OH	42.46 $\pm$ 0.25 ^b	-52.62 $\pm$ 0.25	-53.56 $\pm$ 0.25
C ₃ H ₇ OH	47.50 $\pm$ 0.24 ^b	-57.66 $\pm$ 0.24	-58.80 $\pm$ 0.24
C ₄ H ₉ OH	52.42 $\pm$ 0.26 ^b	-61.69 $\pm$ 0.26	-62.96 $\pm$ 0.27
C ₅ H ₁₁ OH	57.04 $\pm$ 0.17 ^b	-65.03 $\pm$ 0.18	
C ₆ H ₁₃ OH	61.61 $\pm$ 0.19 ^b	-68.02 $\pm$ 0.20	
C ₇ H ₁₅ OH	66.82 $\pm$ 0.20 ^c	-71.69 $\pm$ 0.21	
C ₈ H ₁₇ OH	70.98 $\pm$ 0.42 ^c	-74.35 $\pm$ 0.43	

^a Corrected for the isotopic exchange reactions, see the text.

^b Reference 25

^c Reference 26

TABLE 9. Heat capacity values for some n-alkan-1-ols in H₂O at 298.15 K. The uncertainties are twice the overall standard deviation of the mean, calculated by a semigraphical method.⁽¹⁴⁾

Solute	$\Delta_{\text{sol}}C_{p,m}/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	$C_{p,2}/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$		
		exp ^a	calc. ^b	$\Delta(\text{exp-calc})$
CH ₃ OH	76 $\pm$ 2	157 $\pm$ 2	166	-9
C ₂ H ₅ OH	149 $\pm$ 2	261 $\pm$ 2	256	5
C ₃ H ₇ OH	210 $\pm$ 3	351 $\pm$ 3	346	5
C ₄ H ₉ OH	264 $\pm$ 3	441 $\pm$ 3	436	5
C ₅ H ₁₁ OH	324 $\pm$ 6	532 $\pm$ 6	526	6
C ₆ H ₁₃ OH	375 $\pm$ 4	612 $\pm$ 4	616	-4
C ₇ H ₁₅ OH	426 $\pm$ 6	704 $\pm$ 7	706	-2
C ₈ H ₁₇ OH	475 $\pm$ 7	800 $\pm$ 12	796	4

a. The values are calculated by use of C_p^* values in ref. 26

b. The values are derived by use of an empirical group additivity scheme.⁽²⁸⁾

TABLE 10. Heat capacity values^(a) for some n-alkan-1-ols in D₂O at 298.15 K. The uncertainties are twice the overall standard deviation of the mean, calculated by a semigraphical method.⁽¹⁴⁾

Solute	$\Delta_{\text{sol}}C_{p,m}/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	$C_{p,2}^{\infty}/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$
CH ₃ OH	84 $\pm$ 2	165 $\pm$ 2
C ₂ H ₅ OH	165 $\pm$ 2	277 $\pm$ 2
C ₃ H ₇ OH	233 $\pm$ 2	374 $\pm$ 2
C ₄ H ₉ OH	290 $\pm$ 3	467 $\pm$ 3

a. The values include the contribution from the isotopic exchange reaction.

LEGENDS

- Fig. 1 Second virial coefficients of enthalpy, h_{xx} , versus temperature for some n-alkan-1-ols. (a) in H_2O , (b) in D_2O .
- Fig. 2 Third virial coefficients of enthalpy, h_{xxx} , versus temperature for some n-alkan-1-ols. (a) in H_2O , (b) in D_2O .
- Fig. 3. Enthalpies of solution for n-alkan-1-ols at infinite dilution in H_2O at 288.15 K (■), 298.15 K (▼), 308.15 K (□) and 318.15 K (●), versus the number of carbon atoms, N_C .
- Fig. 4 Enthalpies of solvation for n-alkan-1-ols at infinite dilution in H_2O (●) and in D_2O (□) at 298.15 K versus the number of carbon atoms, N_C . Corrections have been made for the isotopic exchange reaction in D_2O .
- Fig. 5 Partial molar heat capacities for n-alkan-1-ols at infinite dilution in H_2O (●) and in D_2O (□) at 298.15 K versus the number of carbon atoms, N_C . Corrections for the isotopic exchange reaction in D_2O have not been made.

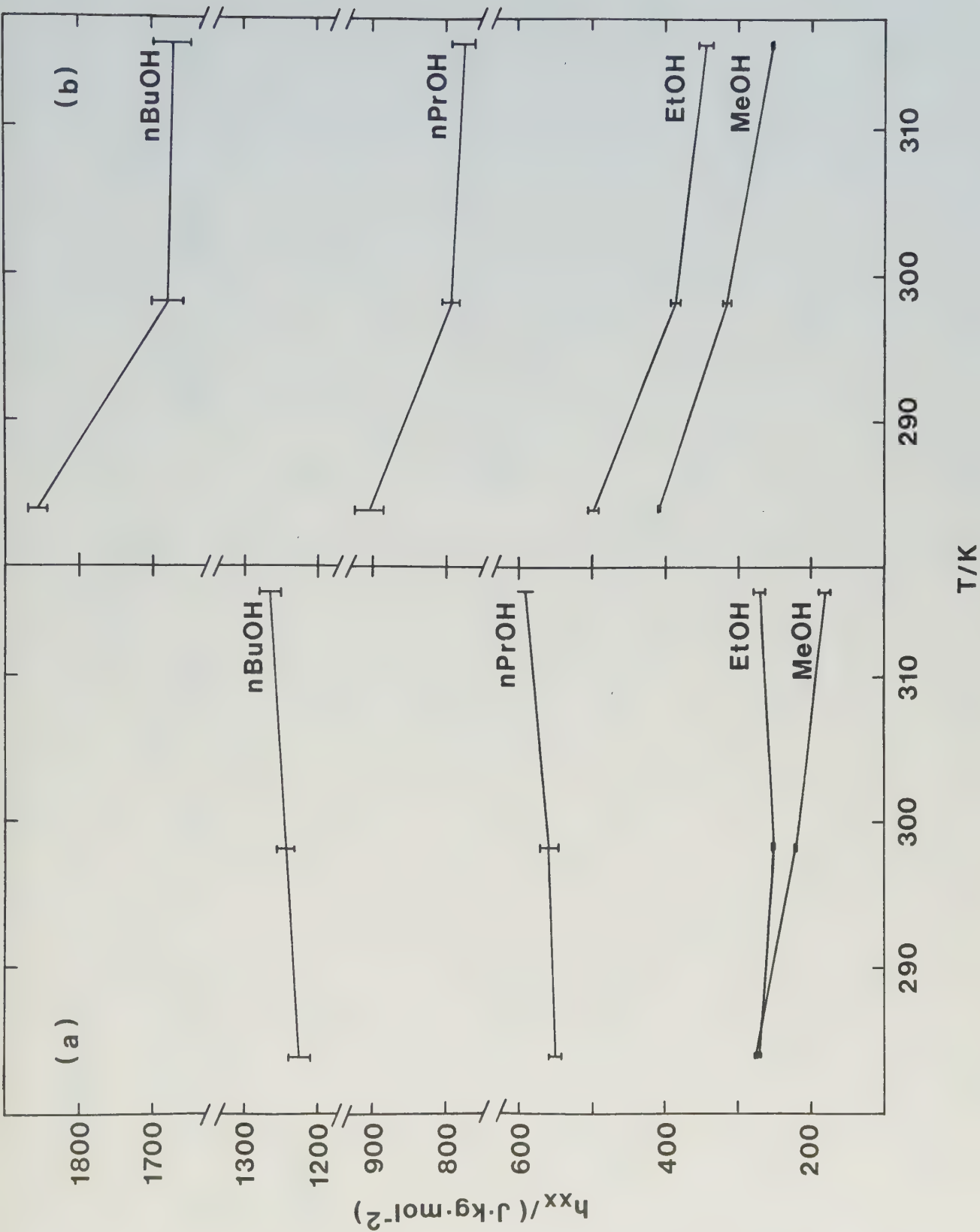


Figure 1

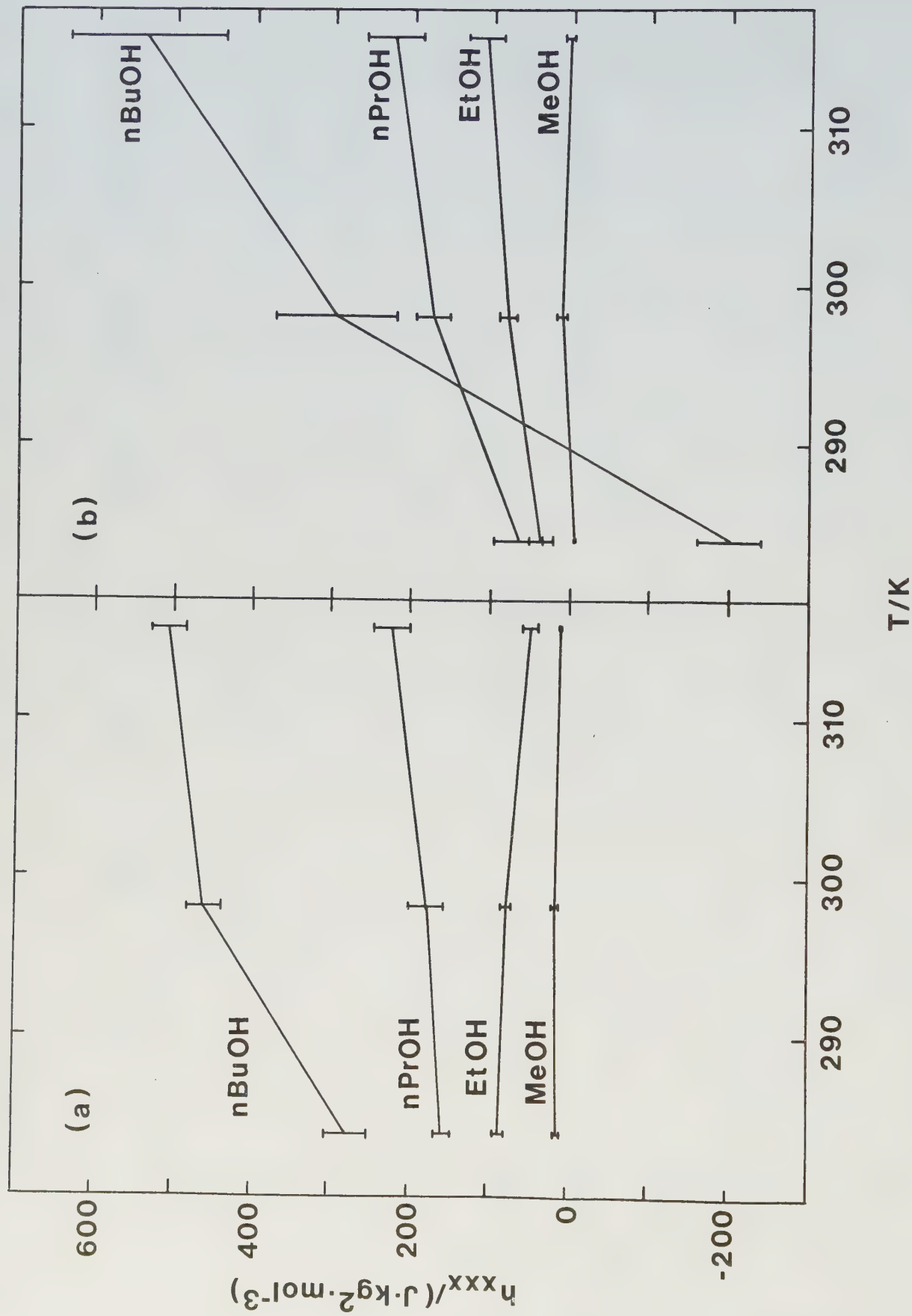


Figure 2

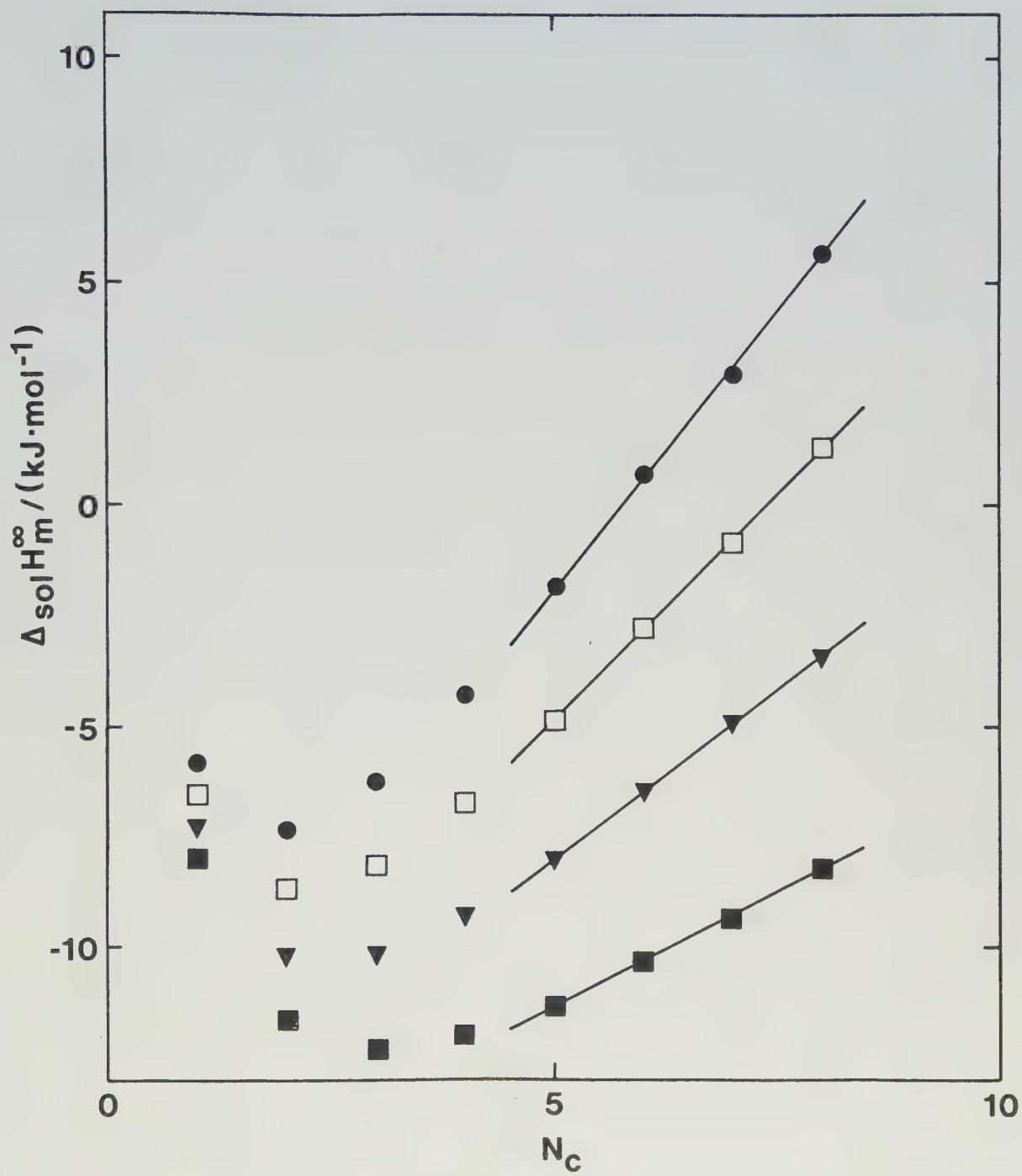


Figure 3

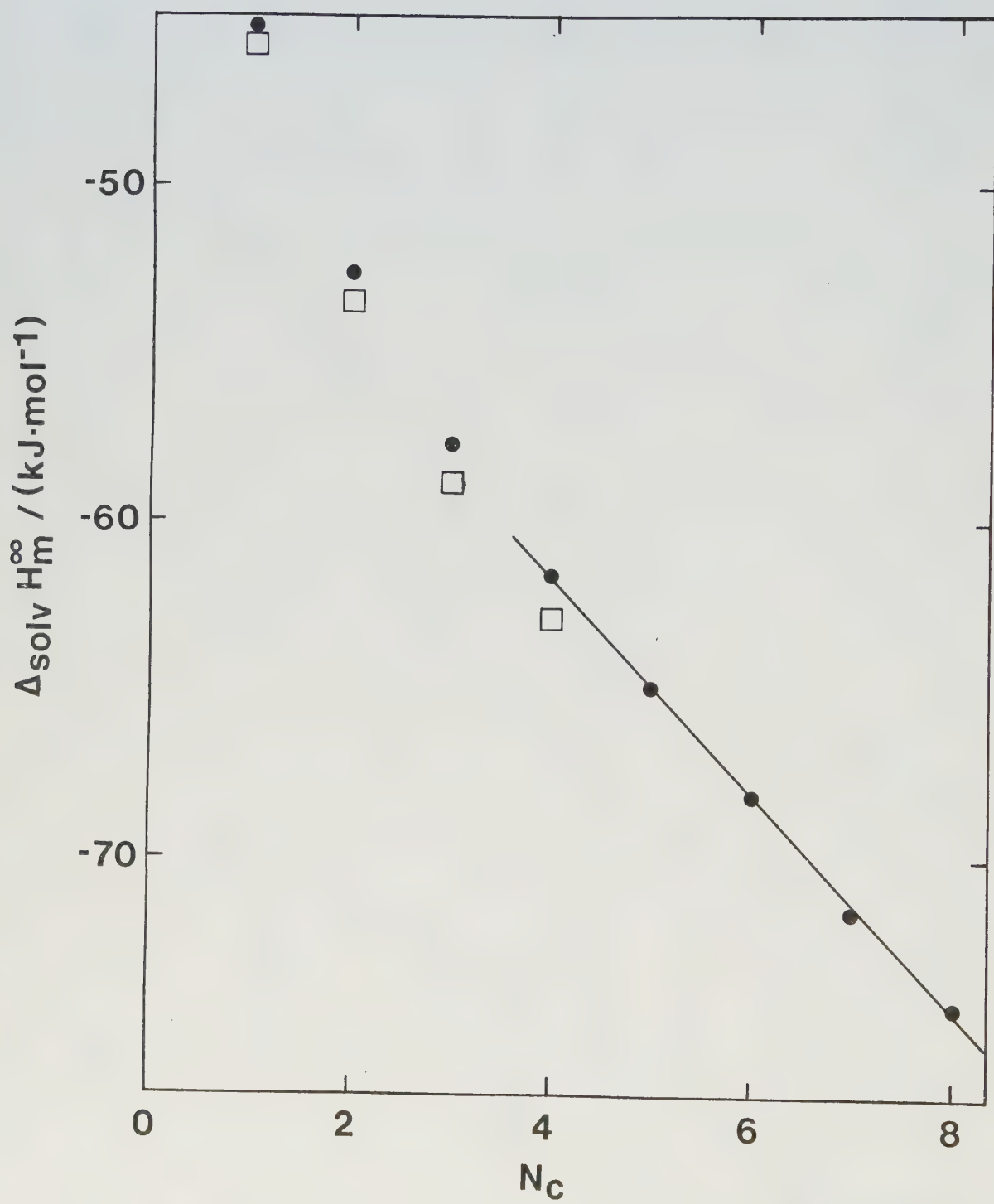


Figure 4

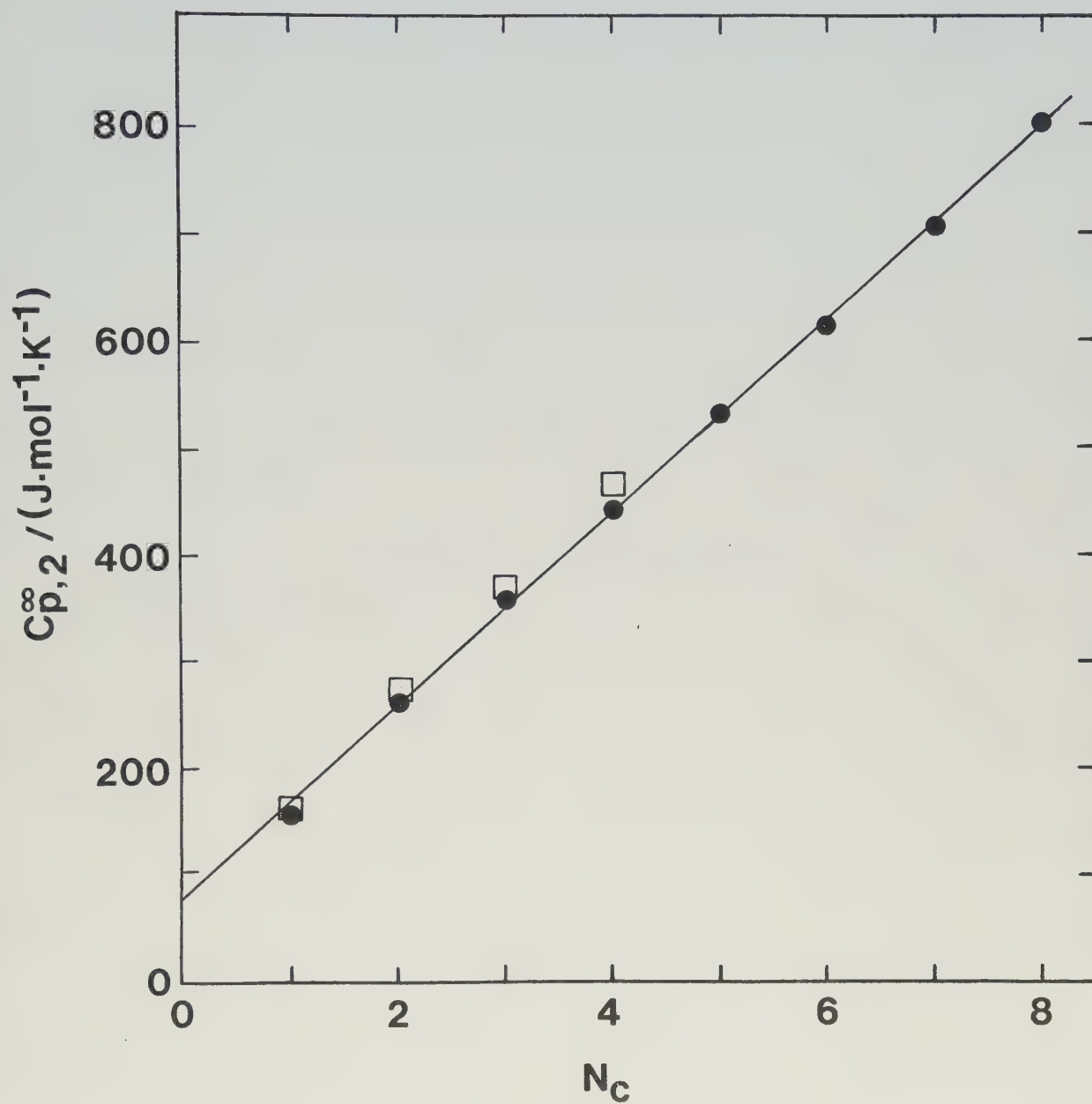


Figure 5

IV

THERMODYNAMIC PROPERTIES FOR SOME MONO-, DI-, AND TRIESTERS.
ENTHALPIES OF SOLUTION IN WATER, 288.15-318.15 K. ENTHALPIES OF
VAPORIZATION AND HEAT CAPACITIES, 298.15 K

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ABSTRACT

Enthalpies of dissolution in water of some monoesters, ethylene-glycol diesters and glycerol triesters have been determined calorimetrically at different temperatures in the range 288-318 K.

Enthalpies of vaporization and heat capacities for the pure compounds have been determined at 298.15 K. Density values determined at 293.15 K and 298.15 K for some of the diesters and triesters are also reported. Values for enthalpies of solvation and for partial molar heat capacities at 298.15 K have been calculated for the infinite dilute solutions. Results are discussed in terms of deviation from empirical additivity schemes.

1. INTRODUCTION

One of the most important structure-forming forces in biology is the "hydrophobic interaction", i.e., the tendency of hydrophobic groups in aqueous solution to aggregate.⁽¹⁾ For instance, the peptide chains of globular proteins tend to be folded in such a way that the hydrophobic parts are concentrated to the interior of the molecule. The lipid bilayers of biological membranes, which are formed by the long alkyl chains of phospholipid molecules, is another example.

Hydrophobic interaction is a consequence of the high Gibbs energy cost for the solvation of hydrophobic compounds or groups in water, "hydrophobic hydration". Other characteristic thermodynamic properties for such processes are their large negative entropy values and large positive changes in heat capacity. Values for the partial molar heat capacity at infinite dilution, $C_{p,2}^{\infty}$, are thus exceptionally large for hydrophobic compounds in water. For instance, $C_{p,2}^{\infty}$ values for hydrocarbons in water are about three times higher than corresponding values for non aqueous solvents. Another interesting feature with $C_{p,2}^{\infty}$ values for simple (non-ionic) hydrophobic compounds in aqueous solution is that they often can be precisely predicted from simple empirical additivity schemes,^(2,3,4) i.e. group contributions are highly additive. This has led to the conclusion that the hydrophobic hydration effect, as reflected by the large heat capacity value, is a short-range effect⁽²⁾ and it has been proposed that the excess heat capacity is connected with temperature dependent structural properties of the first solvation shell around the hydrophobic groups.^(2,5,6)

A decreased contact between the hydrophobic groups and water is expected to lead to a decrease of the excess heat capacity. If this

argument is turned around, one may take a low experimental $C_{p,2}^{\infty}$ value as a sign of intra-molecular hydrophobic interaction. However, such arguments must be used with caution when applied to complex biochemical systems. For instance, it should be noted that exceptionally large $C_{p,2}^{\infty}$ values have been found for sugars and some other polyols in aqueous solution.⁽⁷⁾

The present work is one in a series of calorimetric investigations on the thermodynamic properties of hydrophobic compounds in aqueous solution, cf. reference 8. Here we report results from measurements on methyl- and ethylesters (CH_3OCOR , $\text{C}_2\text{H}_5\text{OCOR}$), ethylene-glycol diesters ($\text{C}_2\text{H}_4(\text{OCOR})_2$) and glycerol triesters ($\text{C}_3\text{H}_5(\text{OCOR})_3$). These compounds may serve as simple models for the hydrophobic part of phospholipids, in which two long-chain fatty acid molecules are connected to glycerol by ester linkages.

A microcalorimetric technique was used to determine enthalpies of solution at infinite dilution at different temperatures. From the temperature dependence, corresponding changes in heat capacity were derived. In addition, enthalpies of vaporization and heat capacities were determined at 298.15 K, leading to values for enthalpies of solvation and partial molar heat capacities. Further, densities were determined for some of the pure compounds. These latter data were needed for the evaluation of the calorimetric dissolution experiments, in which a volumetric injection technique was used.

2. EXPERIMENTAL

Materials

Methylacetate and ethylacetate (Fluka AG for HPLC); ethylpropanoate and ethyleneglycoldiacetate (Kebo); methylbutanoate, ethylbuta-

noate, ethylpentanoate, ethylhexanoate, ethyl-2,2-dimethylpropanoate and triacetin ($\text{C}_3\text{H}_5(\text{OCO}\cdot\text{CH}_3)_3$) (Fluka AG purum); methylhexanoate (Fluka AG puriss) and ethyleneglycoldipropoate, ethyleneglycoldibutanoate, tripropionin ($\text{C}_3\text{H}_5(\text{OCO}\cdot\text{CH}_2\cdot\text{CH}_3)_3$) (prepared by Syntestjänst, Chemical Center, Lund) were all purified by drying with 4A molecular sieves, followed by fractional distillation using a spinning band column. Distillations were performed at reduced pressure, except for methylacetate and ethylacetate. As determined by gas chromatography for all samples, the mass fraction of water was ≤ 0.0002 and the purities were > 99.9 moles per cent. Tributyrin ($\text{C}_3\text{H}_5(\text{OCO}\cdot(\text{CH}_2)_2\cdot\text{CH}_3)_3$) (Fluka AG puriss, > 99 moles per cent by gas chromatography) was used as received. The mass fraction of water was < 0.0003 . Reagent-grade water produced by a Milli-Q filtration system was used.

Density measurements

Densities at 293.15 K and 298.15 K were determined by use of an Anton Paar DMA 60 density meter. Water and nitrogen were used as calibration substances. One experiment was made for each compound and temperature.

Calorimetric dissolution measurements

Enthalpy of solution values were determined by use of an automatic flow-microcalorimetric technique.⁽⁹⁾ Calibrations were performed electrically and by dissolution of propan-1-ol in water at 298.15 K.⁽⁹⁾ The Hamilton syringe used for injections of the solute was thermostated at (297.2 ± 0.1) K. Eight to 10 measurements were normally performed for each compound and temperature.

Methylacetate, ethylacetate, ethylpropanoate, methylbutanoate and ethyleneglycoldiacetate were injected at a low flow rate, about

$0.003 \text{ mm}^3 \cdot \text{s}^{-1}$, in order to be able to consider the final solute concentration as infinitely dilute. At least two different injection periods (normally 600 s and 3000 s) were used in order to allow corrections to be made for small leakage effects from the syringe.⁽⁹⁾ Integration times were 1-2 h. Water flow rate was $11 \text{ mm}^3 \cdot \text{s}^{-1}$. No significant leakage effects were observed for the other compounds, which are very slightly soluble in water. The injection flow rate was about $0.03 \text{ mm}^3 \cdot \text{s}^{-1}$ and the injection periods were in the range 120 to 180 s. Integration times were in the range 2-8 h except for tributyrin.

The low solubility of tributyrin required very long experimental periods and solution enthalpies determined by the use of the instrument described in reference 9 were much less precise than for the other compounds. This became the incitement to undertake a further development of the present calorimetric technique. Results of that work will be reported in detail elsewhere.⁽¹⁰⁾ The values reported here for tributyrin were obtained by use of a new vessel which fits the LKB 4-channel microcalorimeter.⁽¹¹⁾ A spiralized, thin-walled teflon tube is suspended in the water-filled sample cup of an insertion vessel of the type described in reference 12. The sample is injected into the teflon spiral through which water is pumped at a rate of $11 \text{ mm}^3 \cdot \text{s}^{-1}$. The measurement technique is thus very similar to that described in reference 9, but the very stable thermostated water bath ($\pm 1 \times 10^{-4} \text{ K}$) of the 4-channel calorimeter allows significantly longer experimental periods than the earlier instrument.⁽⁹⁾ In the experiments reported here for tributyrin, the time periods needed for dissolution of 4 mm^3 were 10 h (318.15 K) to 20 h (288.15 K).

Heat capacity measurements

Heat capacity values at 298.15 K were determined for some of the pure compounds by use of a drop heat-capacity calorimeter.⁽¹³⁾ The sample ampoule was charged with about 0.6 cm^3 of the liquid substance. No reference ampoule was used. The calorimeter was calibrated with water using the specific heat capacity value of $4.1797 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$ ⁽¹⁴⁾ at 298.15 K. Two to three series each of 8 to 10 measurements were made for each compound.

Calorimetric vaporization measurements

For ethylbutanoate, ethylpentanoate, ethylhexanoate and ethyleneglycoldiacetate, the enthalpy of vaporization measurements were performed by use of a calorimeter described in references 15 and 16. Results reported for the other compounds were determined by use of the Morawetz calorimeter.⁽¹⁷⁾ Normally four to six measurements were made for each compound.

3. RESULTS AND DISCUSSION

Uncertainties

Unless otherwise indicated, uncertainties in values reported in this paper are twice the overall standard deviation of the mean.

Densities

Table 1 shows results of the density measurements. Assuming that the density for impurities deviates by less than 10 per cent from the measured densities, the uncertainties will be less than ± 1 in the last digit presented.

Enthalpies of solution at infinite dilution, $\Delta_{\text{sol}} H_m^\infty$

The values for enthalpy of solution in water were calculated as described in reference 9. Densities used were from this work and from

reference 18. Final concentrations of the esters are less than $0.0032 \text{ mol}\cdot\text{dm}^{-3}$ and the solutions are taken as infinitely dilute. Results are shown in table 2.

In the literature only a few results are reported for enthalpy of solution measurements of esters in water. Della Gatta et al⁽¹⁹⁾ have reported results at 298.15 K for methylacetate $-(7.81 \pm 0.07) \text{ kJ}\cdot\text{mol}^{-1}$ and methylbutanoate $-(8.04 \pm 0.11) \text{ kJ}\cdot\text{mol}^{-1}$. Compared with our results, these values are slightly outside the combined limits of error, being more negative and less negative, respectively.

Enthalpies of vaporization, $\Delta_{\text{vap}}H_m^0$, and of solvation, $\Delta_{\text{solv}}H_m^\infty$.

Solvation enthalpy values were calculated using the equation

$$\Delta_{\text{solv}}H_m^\infty = \Delta_{\text{sol}}H_m^\infty - \Delta_{\text{vap}}H_m^0, \quad (1)$$

where $\Delta_{\text{vap}}H_m^0$ is the enthalpy of vaporization to form the ideal gas. The determined $\Delta_{\text{vap}}H_m^0$ values refer to gas in equilibrium with its liquid phase. However, the difference can in all cases be estimated to be less than 0.1 per cent of the $\Delta_{\text{vap}}H_m^0$ values⁽²⁰⁾ and the experimental $\Delta_{\text{vap}}H_m^0$ values have therefore been taken equal to the $\Delta_{\text{vap}}H_m^0$ values. The $\Delta_{\text{vap}}H_m^0$ values and the calculated $\Delta_{\text{solv}}H_m^\infty$ values at 298.15 K are summarized in table 3.

In figure 1, $\Delta_{\text{solv}}H_m^\infty$ values at 298.15 K are plotted versus the number of alkyl carbon atoms, N_c , for methyl- and ethylesters, the ethyleneglycol diesters and the glycerol triesters. For all four series of compounds, linear relations are found. We note that there is a significant difference between the lines for the methyl- and ethylester series, although their slopes are the same. Della Gatta

et al.⁽¹⁹⁾ have earlier found that branching of the alkyl chain for monoesters leads to less negative values. Our value for ethyl-2,2-dimethylpropanoate agrees with that observation.

The methylesters, ethylesters (except ethyl-2,2-dimethylpropanoate) and ethyleneglycol diesters are all straight chain compounds. For these series, the following values for group contributions to enthalpy of solvation at 298.15 K were derived by use of multiple linear regression:

$$\Delta_{\text{solv}} H_m^\infty(-\text{CH}_2\cdot\text{OCO}-) = -21.43 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{solv}} H_m^\infty(\text{CH}_3\cdot\text{OCO}-) = -28.20 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{solv}} H_m^\infty(-\text{CH}_3) = -12.09 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{solv}} H_m^\infty(-\text{CH}_2-) = -3.61 \text{ kJ}\cdot\text{mol}^{-1}$$

$\Delta_{\text{solv}} H_m^\infty$ values calculated by use of these parameters and the difference between the experimental and the calculated values are also shown in table 3.

The contribution to the $\Delta_{\text{solv}} H_m^\infty$ value from the methylene group, $-3.61 \text{ kJ mol}^{-1}$, is close to the value obtained from measurements on methylesters by Della Gatta et al,⁽¹⁹⁾ $-3.46 \text{ kJ mol}^{-1}$. Their value for solvation of the group $\text{CH}_3\cdot\text{OCO}\dots\text{H}$, $-37.7 \text{ kJ mol}^{-1}$, agrees well with the value which can be derived from the present results, $-36.7 \text{ kJ mol}^{-1}$. The present group value for $-\text{CH}_2-$ is more exothermic than the value we derived for long-chain n-alkan-1-ols ($N_C \geq 4$), -3.2 kJ mol^{-1} .⁽⁸⁾ For short-chain n-alkan-1-ols ($N_C \leq 4$), the $-\text{CH}_2-$ value increases gradually with decreasing chain length and is -7.5 kJ mol^{-1} for the step C_1 to C_2 . The results suggest that the hydroxyl group has a more long range effect on the $\Delta_{\text{solv}} H_m^\infty$ value than the ester group. The $-\text{CH}_2-$ increment for the triesters, -3.9 kJ mol^{-1} , agrees within uncertainty limits

with our results for mono- and diesters.

Heat capacity values

Results from the enthalpy of solution measurements at different temperatures were used to calculate the change in heat capacity in going from the pure compound to the infinitely dilute aqueous solutions, $\Delta_{\text{sol}}C_{p,m}^{\infty}$. The corresponding values for $\Delta_{\text{sol}}H_m^{\infty}$ and T were represented by the equation

$$\Delta_{\text{sol}}H_m^{\infty} = a + bT, \quad (2)$$

and

$$\Delta_{\text{sol}}C_{p,m}^{\infty} = b \quad (3)$$

Heat capacity values for the pure compounds at 298.15 K, $C_{p,m}^*$, were combined with the corresponding $\Delta_{\text{sol}}C_{p,m}^{\infty}$ values to give the partial molar heat capacity values at 298.15 K, $C_{p,2}^{\infty}$.

$$C_{p,2}^{\infty} = C_{p,m}^* + \Delta_{\text{sol}}C_{p,m}^{\infty} \quad (4)$$

Values of $C_{p,m}^*$, $\Delta_{\text{sol}}C_{p,m}^{\infty}$ and $C_{p,2}^{\infty}$ are given in table 4.

Genevieve et al⁽²²⁾ have reported $C_{p,2}^{\infty}$ values at 298.15 K for methylacetate (298 ± 1) J·mol⁻¹·K⁻¹ and for ethylacetate (397 ± 1) J·mol⁻¹·K⁻¹. These values are slightly greater than those reported here.

Different additivity schemes for the calculation of $C_{p,2}^{\infty}$ values at 298.15 K have been proposed.^(2,3,4) We prefer to use our very simple scheme⁽²⁾ and let deviations from the additivity rules indicate an interesting property for the molecule. For the monoesters (except for the branched ethyl-2,2-dimethylpropanoate), we obtain the equation

$$C_{p,2}^{\infty}/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) = 85 N_c + 127 \quad (5)$$

The intercept is equal to

$$2C_{p,2}^{\infty}(-\text{H}) + C_{p,2}^{\infty}(-\text{OCO-}),$$

where $C_{p,2}^{\infty}(-\text{H})$ and $C_{p,2}^{\infty}(-\text{OCO-})$ are the contribution to the $C_{p,2}^{\infty}$ value from a hydrogen atom and an ester group, respectively.

Using the value for $C_{p,2}^{\infty}(-\text{H}) = 67 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$,⁽²⁾ we can calculate $C_{p,2}^{\infty}(-\text{OCO-})$ to be $-7 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. From the slope, we obtain $C_{p,2}^{\infty}(-\text{CH}_2-) = 85 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. The $C_{p,2}^{\infty}$ values calculated by use of these parameters and the differences from the experimental values are given in table 4. The contribution obtained for the methylene group, $85 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, is in good agreement with the values $90 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ (2) and $87.5 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ (4), which are mean values from several homologous series. The ester group parameter agrees well with the value $-10 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ derived by use of our additivity scheme⁽²⁾ from values determined by direct heat capacity measurements.⁽²²⁾ As can be expected,⁽²⁾ the experimental value for the branched ethyl-2,2-dimethylpropanoate is lower than the calculated value. However, the experimental value for ethylhexanoate is also slightly lower than the calculated value, for which we have no explanation.

For the diesters and triesters, the agreement between the experimental and the calculated values is good for the first two compounds in each homologous series. However, negative deviations are found for ethyleneglycoldibutanoate and, in particular, for tributyrin. The main contribution to the $C_{p,2}^{\infty}$ values comes from the hydrophobic part

of the molecule, i.e., the hydrocarbon chains. In figure 2 these contributions, $C_{p,2}^{\infty} - N_{\text{oco}} \cdot C_{p,2}^{\infty} (-\text{OCO}-)$, where N_{oco} is the number of ester groups, is plotted versus the number of hydrogen atoms, N_{H} , cf. references 2 and 5. From the figure 2 it can be seen that a good linear relation is obtained except for tributyrin, for which the point falls significantly outside the line. The deviation corresponds approximately to the hydrophobic hydration value for one methylene group. We interpret the result as a sign of hydrophobic interactions between the rather long alkyl chains.

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REFERENCES

1. Tanford, C. The Hydrophobic Effect: Formation of Micelles and Biological Membranes. 2nd Edition. Wiley-Interscience, New York, 1980.
2. Nichols, N.; Sköld, R.; Spink, C.; Suurkuusk, J.; Wadsö, I. J. Chem. Thermodynamics 1976, 8, 1081.
3. Guthrie, J. P. Can. J. Chem. 1977, 55, 3700.
4. Cabani, S.; Gianni, P.; Lepori, L.; Mollica, V. J. Solution Chem. 1981, 10, 563.
5. Gill, S. J.; Wadsö, I. Proc. Natl. Acad. Sci. 1976, 73, 2955.
6. Dec, S.F.; Gill, S. J.; Olofsson, G.; Wadsö, I. J. Phys. Chem. 1985, 89, 3758.
7. Lian, Y.-N.; Chen, A.-T.; Suurkuusk, J.; Wadsö, I. Acta Chem. Scand. 1982 A36, 735.
8. Hallén, D.; Nilsson, S.-O.; Rothschild, W.; Wadsö, I. J. Chem. Thermodynamics, in press.
9. Nilsson, S.-O.; Wadsö, I. J. Chem. Thermodynamics 1984, 16, 317.
10. Hallén, D., Nilsson, S.-O., Wadsö, I. To be published.
11. Suurkuusk, J.; Wadsö, I. Chemica Scripta 1982, 20, 155.
12. Görman Nordmark, M.; Laynez, J.; Schön, A.; Suurkuusk, J.; Wadsö, I. J. Biochem. Biophys. Methods 1984, 10, 187.
13. Suurkuusk, J.; Wadsö, I. J. Chem. Thermodynamics 1974, 6, 667.
14. Osborne, N.S.; Stimson, H. F.; Ginnings, D. C. J. Res. Nat. Bur. Stand. 1939, 23, 197.
15. Wadsö, I. Acta Chem. Scand. 1966, 20, 536.
16. Wadsö, I. Acta Chem. Scand. 1968, 22, 2438.
17. Morawetz, E. Chemica Scripta 1971, 1, 103.
18. Selected Values of Properties of Hydrocarbons and Related Compounds. API Research project 44, Thermodynamic Research Center, Department of Chemistry, Texas University, College Station, Texas 1970.

19. Della Gatta, G.; Stradella, L.; Venturello, P. J. Solution Chem. 1981, 10, 203.
20. Majer, V.; Svoboda, V. Enthalpies of Vaporization of Organic Compounds. Chemical Data Series No. 32. Blackwell Scientific Publications, Oxford, 1985.
21. Månsson, M.; Sellers, P.; Stridh, G.; Sunner, S. J. Chem. Thermodynamics 1977, 9, 91.
22. Genevieve, R.; Perron, G.; Desnoyers, J. E. Can. J. Chem. 1978, 56, 2808.

TABLE 1. Densities for some esters

Compound	$\rho/(\text{g}\cdot\text{cm}^{-3})$	
	293.15 K	298.15 K
$\text{C}_2\text{H}_4\cdot(\text{OCO}\cdot\text{CH}_2\cdot\text{CH}_3)_2$	1.0420	1.0366
$\text{C}_2\text{H}_4\cdot(\text{OCO}\cdot(\text{CH}_2)_2\cdot\text{CH}_3)_2$	1.0001	0.9953
$\text{C}_3\text{H}_5\cdot(\text{OCO}\cdot\text{CH}_3)_3$	1.1581	1.1527
$\text{C}_3\text{H}_5\cdot(\text{OCO}\cdot\text{CH}_2\cdot\text{CH}_3)_3$	1.0813	1.0763
$\text{C}_3\text{H}_5\cdot(\text{OCO}\cdot(\text{CH}_2)_2\cdot\text{CH}_3)_3$	1.032	1.029

TABLE 2. Enthalpies of solution in water, at infinite dilution, for some esters.

Compound	$\Delta_{\text{sol}} H_m^\infty / (\text{kJ} \cdot \text{mol}^{-1})$			
	288.15 K	298.15 K	308.15 K	318.15 K
$\text{CH}_3 \cdot \text{OCO} \cdot \text{CH}_3$	- 9.09 $\pm$ 0.04	- 7.60 $\pm$ 0.03	- 6.17 $\pm$ 0.04	- 4.62 $\pm$ 0.03
$\text{C}_2\text{H}_5 \cdot \text{OCO} \cdot \text{CH}_3$	- 11.84 $\pm$ 0.05	- 9.69 $\pm$ 0.04	- 7.49 $\pm$ 0.05	- 5.38 $\pm$ 0.08
$\text{CH}_3 \cdot \text{OCO} \cdot (\text{CH}_2)_2 \cdot \text{CH}_3$	- 10.96 $\pm$ 0.05	- 8.33 $\pm$ 0.05	- 5.67 $\pm$ 0.03	- 3.13 $\pm$ 0.04
$\text{C}_2\text{H}_5 \cdot \text{OCO} \cdot \text{CH}_2 \cdot \text{CH}_3$	- 12.97 $\pm$ 0.08	- 10.25 $\pm$ 0.04	- 7.47 $\pm$ 0.05	- 4.75 $\pm$ 0.07
$\text{C}_2\text{H}_5 \cdot \text{OCO} \cdot (\text{CH}_2)_2 \cdot \text{CH}_3$	- 13.27 $\pm$ 0.06	- 9.89 $\pm$ 0.04	- 6.70 $\pm$ 0.03	- 3.45 $\pm$ 0.04
$\text{CH}_3 \cdot \text{OCO} \cdot (\text{CH}_2)_4 \cdot \text{CH}_3$	- 10.58 $\pm$ 0.10	- 6.70 $\pm$ 0.03	- 2.97 $\pm$ 0.04	0.70 $\pm$ 0.08
$\text{C}_2\text{H}_5 \cdot \text{OCO} \cdot (\text{CH}_2)_3 \cdot \text{CH}_3$	- 13.28 $\pm$ 0.09	- 9.51 $\pm$ 0.09	- 5.41 $\pm$ 0.06	- 1.70 $\pm$ 0.03
$\text{C}_2\text{H}_5 \cdot \text{OCO} \cdot \text{C}(\text{CH}_3)_3$	- 12.73 $\pm$ 0.08	- 9.03 $\pm$ 0.04	- 5.22 $\pm$ 0.04	- 1.69 $\pm$ 0.06
$\text{C}_2\text{H}_5 \cdot \text{OCO} \cdot (\text{CH}_2)_4 \cdot \text{CH}_3$	- 12.78 $\pm$ 0.23	- 8.45 $\pm$ 0.16	- 4.37 $\pm$ 0.14	- 0.32 $\pm$ 0.32
$\text{C}_2\text{H}_4 \cdot (\text{OCO} \cdot \text{CH}_3)_2$	- 7.57 $\pm$ 0.05	- 5.62 $\pm$ 0.05	- 3.61 $\pm$ 0.02	- 1.76 $\pm$ 0.01
$\text{C}_2\text{H}_4 \cdot (\text{OCO} \cdot \text{CH}_2 \cdot \text{CH}_3)_2$	- 10.72 $\pm$ 0.04	- 7.62 $\pm$ 0.04	- 4.62 $\pm$ 0.02	- 1.69 $\pm$ 0.02
$\text{C}_2\text{H}_4 \cdot (\text{OCO} \cdot (\text{CH}_2)_2 \cdot \text{CH}_3)_2$	- 11.08 $\pm$ 0.06	- 7.26 $\pm$ 0.09	- 3.21 $\pm$ 0.06	0.80 $\pm$ 0.05
$\text{C}_3\text{H}_5 \cdot (\text{OCO} \cdot \text{CH}_3)_3$	- 5.95 $\pm$ 0.03	- 3.56 $\pm$ 0.02	- 1.00 $\pm$ 0.01	1.39 $\pm$ 0.04
$\text{C}_3\text{H}_5 \cdot (\text{OCO} \cdot \text{CH}_2 \cdot \text{CH}_3)_3$	- 10.46 $\pm$ 0.05	- 6.84 $\pm$ 0.06	- 2.69 $\pm$ 0.03	1.42 $\pm$ 0.05
$\text{C}_3\text{H}_5 \cdot (\text{OCO} \cdot (\text{CH}_2)_2 \cdot \text{CH}_3)_3$	- 10.38 $\pm$ 0.54	- 5.57 $\pm$ 0.20	- 0.82 $\pm$ 0.15	4.26 $\pm$ 0.11

TABLE 3. Enthalpies of vaporization, $\Delta_{\text{vap}}H_m^0$, and enthalpies of solvation in water at infinite dilution, $\Delta_{\text{sol}V}H_m^0$, for some esters at 298.15 K. Calculated values were obtained from the parameters for unbranched compounds (cf. the text).

Compounds	$\Delta_{\text{vap}}H_m^0$		$\Delta_{\text{sol}V}H_m^0/(\text{kJ}\cdot\text{mol}^{-1})$	
	$\text{kJ}\cdot\text{mol}^{-1}$	exp	calc	exp - calc
$\text{CH}_3\cdot\text{OCO}\cdot\text{CH}_3$	32.50 ± 0.16^a	-40.10 ± 0.17^d	-40.29	0.19
$\text{C}_2\text{H}_5\cdot\text{OCO}\cdot\text{CH}_3$	35.69 ± 0.18^a	-45.38 ± 0.19^d	-45.61	0.23
$\text{CH}_3\cdot\text{OCO}\cdot(\text{CH}_2)_2\cdot\text{CH}_3$	39.33 ± 0.30^a	-47.66 ± 0.31^d	-47.51	-0.15
$\text{C}_2\text{H}_5\cdot\text{OCO}\cdot\text{CH}_2\cdot\text{CH}_3$	39.27 ± 0.20^a	-49.52 ± 0.21^d	-49.22	-0.30
$\text{C}_2\text{H}_5\cdot\text{OCO}\cdot(\text{CH}_2)_2\cdot\text{CH}_3$	42.68 ± 0.10^b	-52.57 ± 0.11	-52.83	0.26
$\text{CH}_3\cdot\text{OCO}\cdot(\text{CH}_2)_4\cdot\text{CH}_3$	48.04 ± 0.12^c	-54.74 ± 0.12	-54.73	-0.01
$\text{C}_2\text{H}_5\cdot\text{OCO}\cdot(\text{CH}_2)_3\cdot\text{CH}_3$	47.01 ± 0.10^b	-56.52 ± 0.14	-56.44	-0.08
$\text{C}_2\text{H}_5\cdot\text{OCO}\cdot\text{C}(\text{CH}_3)_3$	41.29 ± 0.42^a	-50.32 ± 0.43^d	-	-
$\text{C}_2\text{H}_5\cdot\text{OCO}\cdot(\text{CH}_2)_4\cdot\text{CH}_3$	51.72 ± 0.10^b	-60.17 ± 0.19	-60.05	-0.12
$\text{C}_2\text{H}_4\cdot(\text{OCO}\cdot\text{CH}_3)_2$	61.44 ± 0.15^b	-67.06 ± 0.16	-67.04	-0.02
$\text{C}_2\text{H}_4(\text{OCO}\cdot\text{CH}_2\cdot\text{CH}_3)_2$	67.59 ± 0.50^b	-75.21 ± 0.51	-74.26	-0.95
$\text{C}_2\text{H}_4\cdot(\text{OCO}\cdot(\text{CH}_2)_2\cdot\text{CH}_3)_2$	73.21 ± 0.60^b	-80.47 ± 0.61	-81.48	1.01
$\text{C}_3\text{H}_5\cdot(\text{OCO}\cdot\text{CH}_3)_3$	85.74 ± 0.30^b	-89.30 ± 0.31	-	-

cont.

TABLE 3, cont.

$C_3H_5 \cdot (OCO \cdot CH_2 \cdot CH_3)_3$	91.36 $\pm$ 0.40 ^b	-98.20 $\pm$ 0.41	-
$C_3H_5 \cdot (OCO \cdot (CH_2)_2 \cdot CH_3)_3$	107.1 $\pm$ 1.0 ^b	-112.7 $\pm$ 1.2	-

a Reference 20. The uncertainties are estimates.

b This work

c Reference 21.

d The uncertainties are estimates.

TABLE 4 Heat capacities for some esters at 298.15 K. $C_{p,m}^*$ is the molar heat capacity for the pure compounds; $\Delta_{sol}C_{p,m}^\infty$ is the heat capacity change for the aqueous solution process and $C_{p,2}^\infty(\text{exp})$ is the corresponding partial molar heat capacity in the infinitely dilute aqueous solution. $C_{p,2}^\infty(\text{calc})$ is the calculated partial molar heat capacity based on the group parameter values, cf. the text.

Compound	$\frac{C_{p,m}^*}{\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}}$	$\frac{\Delta_{sol}C_{p,m}^\infty}{\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}}$	$\frac{C_{p,2}^\infty}{\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}}$	
			exp	calc exp-calc
$\text{CH}_3\cdot\text{OCO}\cdot\text{CH}_3$	143.9 ^a	148 $\pm$ 3	292 $\pm$ 3	297 - 5
$\text{C}_2\text{H}_5\cdot\text{OCO}\cdot\text{CH}_3$	170.6 ^a	215 $\pm$ 3	386 $\pm$ 3	382 4
$\text{CH}_3\cdot\text{OCO}\cdot(\text{CH}_2)_2\cdot\text{CH}_3$	200.8 ^a	261 $\pm$ 4	462 $\pm$ 4	467 - 5
$\text{C}_2\text{H}_5\cdot\text{OCO}\cdot\text{CH}_2\cdot\text{CH}_3$	197.6 ^a	274 $\pm$ 3	472 $\pm$ 3	467 5
$\text{C}_2\text{H}_5\cdot\text{OCO}\cdot(\text{CH}_2)_2\cdot\text{CH}_3$	225.7 ^a	327 $\pm$ 6	552 $\pm$ 6	552 0
$\text{CH}_3\cdot\text{OCO}\cdot(\text{CH}_2)_4\cdot\text{CH}_3$	257.9 ^a	373 $\pm$ 8	631 $\pm$ 8	637 - 6
$\text{C}_2\text{H}_5\cdot\text{OCO}\cdot(\text{CH}_2)_3\cdot\text{CH}_3$	257.5 ^a	388 $\pm$ 10	646 $\pm$ 10	637 9
$\text{C}_2\text{H}_5\cdot\text{OCO}\cdot\text{C}(\text{CH}_3)_3$	251.3 $\pm$ 0.2 ^b	370 $\pm$ 8	622 $\pm$ 8	637 -15
$\text{C}_2\text{H}_5\cdot\text{OCO}\cdot(\text{CH}_2)_4\cdot\text{CH}_3$	289.3 ^a	415 $\pm$ 10	704 $\pm$ 11	722 -18
$\text{C}_2\text{H}_4\cdot(\text{OCO}\cdot\text{CH}_3)_2$	269.2 $\pm$ 0.2 ^b	194 $\pm$ 5	464 $\pm$ 5	460 4

TABLE 4, cont.

$C_2H_4 \cdot (OCO \cdot CH_2 \cdot CH_3)_2$	331.8 $\pm$ 0.2 ^b	301 $\pm$ 6	633 $\pm$ 6	630	3
$C_2H_4 \cdot (OCO \cdot (CH_2)_2 \cdot CH_3)_2$	380.3 $\pm$ 0.2 ^b	396 $\pm$ 10	776 $\pm$ 10	800	-24
$C_3H_5 \cdot (OCO \cdot CH_3)_3$	389.0 $\pm$ 0.2 ^b	246 $\pm$ 5	635 $\pm$ 5	623	12
$C_3H_5 \cdot (OCO \cdot CH_2 \cdot CH_3)_3$	481.3 $\pm$ 0.3 ^b	398 $\pm$ 18	879 $\pm$ 18	878	1
$C_3H_5 \cdot (OCO \cdot (CH_2)_2 \cdot CH_3)_3$	555.3 $\pm$ 0.3 ^b	487 $\pm$ 27	1042 $\pm$ 27	1133	-91

^a Ref. 18

^b This work.

LEGENDS

- Fig. 1 Enthalpies of solvation for some esters at infinite dilution in H_2O at 298.15 K versus the number of alkyl carbon atoms, N_{C} .
Methylesters (∇), ethylesters ($\bullet$), branched ethylester ($\blacktriangle$), diesters ($\square$) and triesters ($\blacksquare$).
- Fig. 2 Partial molar heat capacities for some esters at infinite dilution in H_2O at 298.15 K, $C_{\text{p},2}^{\infty}$, except the contribution from the ester groups ($N_{\text{OCO}} \cdot C_{\text{p},2}^{\infty}(\text{OCO})$, cf. the text) versus the number of hydrogen atoms, N_{H} .
Methylesters (∇), ethylesters ($\bullet$), branched ethylester ($\blacktriangle$), diesters ($\square$) and triesters ($\blacksquare$).

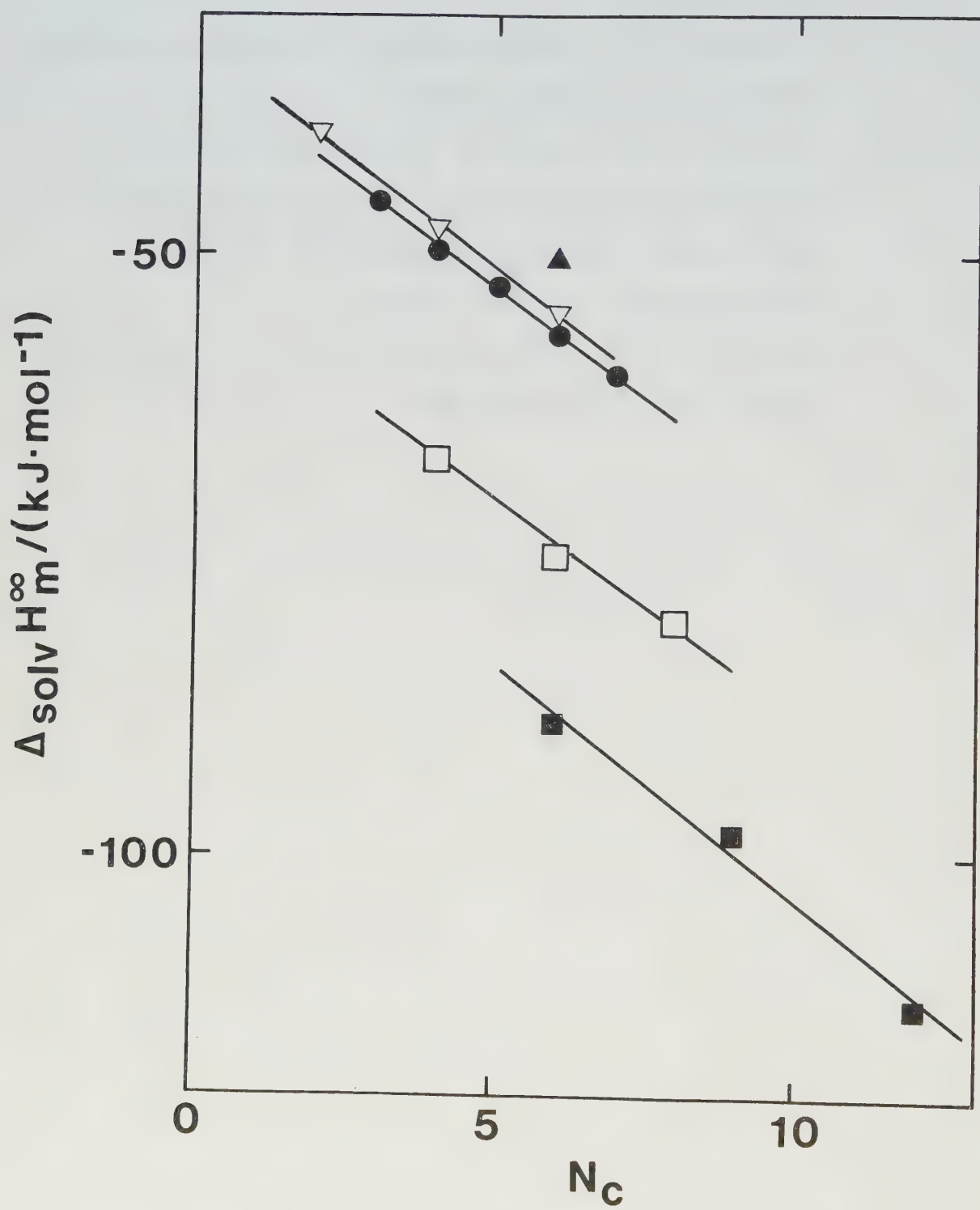


Figure 1

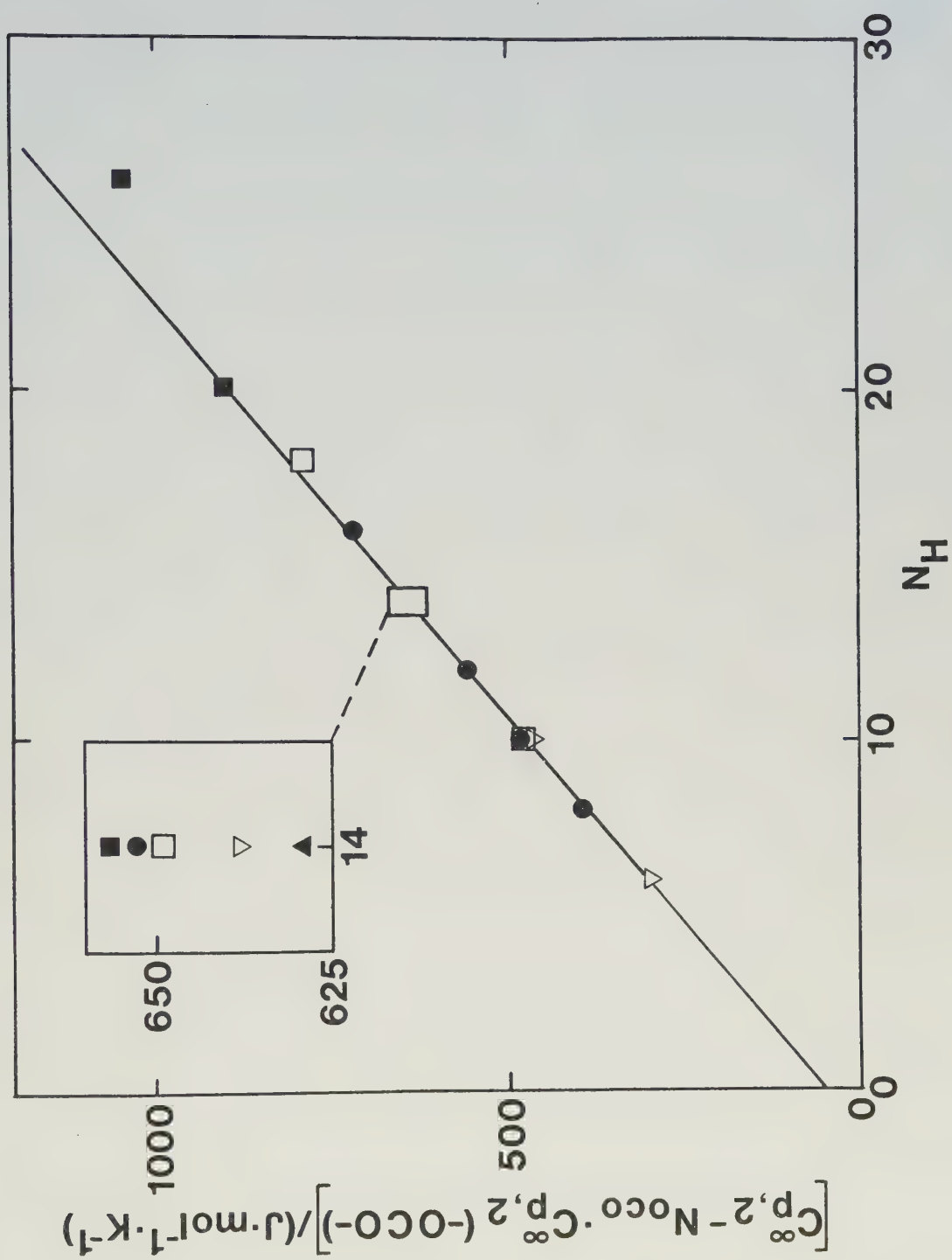


Figure 2

V

Enthalpies of solution of water in benzene and in some n-alkanes

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Short title: $\Delta_{\text{sol}}H_{\text{m}}$ of water in benzene and n-alkanes

ABSTRACT

Enthalpies of dissolution of water in benzene and in some n-alkanes (C_7 , C_8 , C_{10} and C_{12}) have been determined calorimetrically at 298.15 K. In addition, measurements were performed with benzene at 308.07 K and n-decane at 313.14 K. An equation has been derived which describes the solubility of water in n-alkanes as a function of temperature and number of carbon atoms.

1. Introduction

In a series of papers from this laboratory, the solution properties for simple nonionic compounds have been investigated by different calorimetric techniques.⁽¹⁻³⁾ These studies have at least partly been motivated by the need for such model compound studies in biothermodynamics.⁽⁴⁻⁶⁾

In the present paper, a microcalorimetric method is described by which the enthalpy of solution of water into hydrophobic liquids can be measured. The method has been applied on benzene and some n-alkanes.

In our recent microcalorimetric studies^(3,7) of dissolution of slightly soluble compounds, samples were injected into the reaction vessel of the calorimeter, where they were dissolved by a flow of water. Immediately after the injection, a fast endothermic process was always observed for the least soluble compounds. This first phase of the measured process was identified as the dissolution of water into the dry sample. The observations led to the following measurement technique.

A small syringe was charged with a hydrocarbon sample. Its water content was measured by injection into a gas chromatograph. Samples were then injected into the reaction vessel of a microcalorimeter which contained an equilibrium mixture of the same hydrocarbon and water. The enthalpy change measured thus referred to the transfer of water into the hydrocarbon phase until it became saturated with water, whereas no hydrocarbon was dissolved in the water. However, a small amount of hydrocarbon will separate from the transferred water. This amount of hydrocarbon is orders of magnitude smaller than the transferred water and the thermal effect will thus be negligible.

A plot was made of the corresponding enthalpy changes $\Delta_{\text{sol}}H$ against the time integrals A from the g. c. As A is proportional to the water content, extrapolation to $A = 0$ corresponds to the $\Delta_{\text{sol}}H$ value for dry hydrocarbon. The molar enthalpy of solution $\Delta_{\text{sol}}H_m$ has been derived using the literature value for water solubility.

2. Experimental

Benzene (B. D. H. AnalaR) was dried over 4A molecular sieves for several hours and was then fractionally distilled. As judged by gas chromatography, the purity was better than 99.5 moles per cent. N-heptane (B. D. H., better than 99.5 moles per cent), n-octane (SIGMA, about 99 moles per cent), n-decane (SIGMA, about 99 moles per cent) and n-dodecane (SIGMA, about 99 moles per cent) were all used without further purification and were kept over 4A molecular sieves. Reagent-grade H_2O produced by a Milli-Q filtration system was used.

A Varian 3700 g. c. was used for the water-content determinations. The column was packed with porapak Q 80 to 100 mesh, and the hydrogen gas flow rate was $0.4 \text{ cm}^3 \cdot \text{s}^{-1}$.

With the exception of the dissolution-tube systems, the calorimetric setup is identical to that described in reference 8. Figure 1 shows a section through the reaction vessel containing the dissolution tube system made from stainless-steel tubes. After a vertical part, the first tube (i.d. 1.1 mm) is formed into a spiral. The end of that spiral is soldered to a second steel tube (i.d. 0.7 mm) at f. After another vertical part, a second outer spiral is formed which leads to the annular space between the two glass tubes a and b. The space between the brass cup e and the spiral system is

filled with Wood's metal. Two calibration heaters i and n, which are embedded in Wood's metal, are like that described in reference 8. Injections were made by use of 500 mm³, or in some cases 100 mm³, syringes with permanently fixed hypodermic needles.⁽⁸⁾

Hydrocarbon samples of different water concentrations were prepared by mixing the dried hydrocarbon and water-saturated hydrocarbon. Integrals related to the water content were determined in triplicates by g. c. for each syringe filling. This determination was made before and after the calorimetric measurements so as to control that the water content was constant. In order to keep the conditions constant, the g. c. was never switched off during the measurements on each hydrocarbon.

Before beginning of measurements of a new hydrocarbon, the calorimeter flow line was rinsed with ethanol followed by water, until a stable baseline was obtained. The water flow was stopped and 0.5 cm³ of the hydrocarbon was injected into the reaction zone so as to derive the described equilibrated two-phase system.

Normally seven injections were then made into the calorimeter. The injection period was 1500 s and the injection rate was about 0.03 mm³·s⁻¹. The calorimeter tubing system was open at the outlet side. Electrical calibrations were performed by use of the central heater n, and a microprocessor was used to regulate the switching times and to compute the time integrals.

3. Results and discussion

Tables 1 and 2 give the results from determinations of the corresponding enthalpy change $\Delta_{\text{sol}}H$, and the time integral A for the water content. Figures 2 and 3 show plots of $\Delta_{\text{sol}}H$ against A for

benzene and n-alkanes, respectively. It is seen that linear relations are obtained in all cases. Intercepts $\Delta_{\text{sol}}H_{\text{int}}$ were derived by linear regression. The values are the enthalpy changes for the process where the injected mass m_{HC} of dry hydrocarbon is saturated with water.

The molar enthalpy change $\Delta_{\text{sol}}H_m$ for solution of water in the hydrocarbon is calculated by use of equation (1):

$$\Delta_{\text{sol}}H_m = M\Delta_{\text{sol}}H_{\text{int}}/w\rho(dV/dt)t, \quad (1)$$

where M is the molar mass of water, w is the mass fraction of water at saturation, ρ is the density of the hydrocarbon at the temperature 297.2 K of the syringe holder, dV/dt is the volume displacement rate of the syringe and t is the injection time.

The solubility value used for water in benzene is the mean value from references 9 to 11 at 298.15 K and from references 9 and 11 at 308.15 K. The mean values used are believed to be accurate within 1 per cent. The values used for the solubilities in n-alkanes⁽¹²⁾ are believed to be accurate to 3 per cent at 298.15 K and 1 per cent at 313.14 K. Densities were taken from reference 13.

From the linear relations found in figures 2 and 3 we conclude that the integral $\Delta_{\text{sol}}H_m$ values are equal to the partial molar enthalpies in the whole concentration range. Therefore the $\Delta_{\text{sol}}H_m$ values are identical to the molar enthalpy of solution values at infinite dilution $\Delta_{\text{sol}}H_m^\infty$.

Table 3 summarizes values for w , $\Delta_{\text{sol}}H_{\text{int}}$ and $\Delta_{\text{sol}}H_m$. The

uncertainties given are estimates, where the uncertainties given for $\Delta_{\text{sol}}H_m$ include contributions estimated for the volume displacement rate, the electrical calibration constant⁽⁸⁾ (1 per cent) and for impurities.

Experiments with benzene at 298.15 K were performed with 100 or 500 mm³ syringes. The results are in good agreement, but it is seen that larger injections give higher precision. The $\Delta_{\text{sol}}H_m$ value at 308.07 K is not significantly different from the results at 298.15 K, i.e. the $\Delta_{\text{sol}}C_{p,m}$ value is close to zero.

From calorimetric measurements of dissolution of water in benzene at 298.15 K, enthalpy changes are reported by Franks et al.,⁽¹⁴⁾ $(24.6 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1}$, and by De Lisi et al.,⁽¹⁵⁾ $(20.7 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$. The latter value is very different from our results. The value reported by Franks et al. agrees well with the present results, but these workers used a 20 per cent lower value for the water solubility. From a least-square fit of results of solubility measurements in the temperature range 283 to 323 K, Moule et al.⁽¹¹⁾ reported a value of $20.1 \text{ kJ}\cdot\text{mol}^{-1}$ for transfer of 1 mole of water from the benzene phase to the vapor phase. This value corresponds to $24.0 \text{ kJ}\cdot\text{mol}^{-1}$ for dissolution of 1 mole of water in benzene. From solubility measurements in the range 288 to 308 K, Karlsson⁽⁹⁾ reports $\Delta_{\text{sol}}H_m(\text{van't Hoff}) = 23.4 \text{ kJ}\cdot\text{mol}^{-1}$. The values agree within uncertainty limits with the present results.

The $\Delta_{\text{sol}}H_m$ values obtained for the n-alkanes are identical within uncertainty limits. At 298.15 K the mean value is (34.9 ± 1.6)

$\text{kJ}\cdot\text{mol}^{-1}$.[†] From very careful solubility measurements at 298.15 and 313.15 K by Schatzberg,⁽¹²⁾ $\Delta_{\text{sol}}H_{\text{m}}$ (van't Hoff) values for the n-alkanes (C_{10} to C_{13} and C_{16}) were obtained. The mean value, $(34.3 \pm 1.6) \text{ kJ}\cdot\text{mol}^{-1}$, is in very good agreement with the present calorimetric results. Franks et al.⁽¹⁴⁾ reported a very low enthalpy value from calorimetric dissolution measurements of water in n-hexane at 298.15 K, $(8.4 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$. The present results from measurements on n-decane at different temperatures indicate that the $\Delta_{\text{sol}}C_{\text{p,m}}$ value is close to zero.

The lower enthalpy value for dissolution of water in benzene, in comparison with n-alkanes, supports the view that water forms hydrogen bonds to the Π -electron system in benzene.^(16,17)

The constant enthalpy values for the different n-alkanes and the low $\Delta_{\text{sol}}C_{\text{p,m}}$ value lead to the possibility of predicting the water solubility at different temperatures. Starting with the equation:

$$\ln \{K(T)/K(T_0)\} = - (\Delta_{\text{sol}}H_{\text{m}}/R)(1/T - 1/T_0), \quad (2)$$

where K is the equilibrium constant, R is the gas constant and T is the temperature, K can be substituted by the mole fraction X of water. Schatzberg⁽¹²⁾ obtained a linear relation when he plotted $\ln X$ against the molar mass for the n-alkanes (C_7 to C_{16}) at 298.15 and 313.15 K. A linear relationship will thus be obtained when $\ln X$ is plotted against the number N_{C} of carbon atoms:

$$\ln X = mN_{\text{C}} + l, \quad (3)$$

[†] Uncertainty given is twice the standard deviation of the mean

where m and l are constants. From equations (2) and (3) the following equation is derived :

$$X(N_c, T) = \exp\{mN_c - (\Delta_{sol}H_m/R)(1/T) + l + \Delta_{sol}H_m/RT_0\}. \quad (4)$$

For $T_0 = 298.15$ K, the constants m and l are obtained from a plot of $\ln X$ against N_c for results given in reference 12. Insertion of these constants and the calorimetric value for $\Delta_{sol}H_m$ into equation (4) lead to equation (5):

$$X(N_c, T) = \exp\{0.0308N_c - 4.198 \times 10^3 (K/T) + 6.301\}. \quad (5)$$

The values calculated by use of this equation deviate from the experimental values⁽¹²⁾ with a mean deviation of 2 per cent for the hydrocarbons C_7 to C_{16} at 298.15 and 313.15 K. For n-hexane, a calculated value of 5.03×10^{-4} is obtained at 298.15 K, slightly higher than the value 4.76×10^{-4} obtained by Roddy et al.⁽¹⁰⁾ This reference also gives an interpolated value of 5.6×10^{-4} from solubility measurements by Englin et al.,⁽¹⁸⁾ and a mean value of 5.0×10^{-4} from other works reported since 1954.

The uncertainty in the derived X -values due to possible error in $\Delta_{sol}H_m$ will increase with the deviation in temperature ΔT from 298.15 K. For instance, these uncertainties in X are estimated to be 3 per cent at $\Delta T = 15$ K and 7 per cent at $\Delta T = 35$ K.

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REFERENCES

1. Nichols, N.; Sköld, R.; Spink, C.; Suurkuusk, J.; Wadsö, I. J. Chem. Thermodynamics 1976, 8, 1081.
2. Olofsson, G.; Oshodi, A. A.; Qvarnström, E.; Wadsö, I. J. Chem. Thermodynamics 1984, 16, 1041.
3. Nilsson, S.-O.; Wadsö, I. J. Chem. Thermodynamics, in press.
4. Franks, F. Biochemical Thermodynamics. Jones, M. N.: editor. Chapter 2. Elsevier: Amsterdam. 1979.
5. Wadsö, I. Pure and Appl. Chem. 1983, 55, 515.
6. Tanford, C. The Hydrophobic Effect. Formation of Micelles and Biological Membranes. 2nd edition. Wiley-Interscience: New York. 1980.
7. Hallén, D.; Nilsson, S.-O.; Rothschild, W.; Wadsö, I. J. Chem. Thermodynamics, in press.
8. Nilsson, S.-O.; Wadsö, I. J. Chem. Thermodynamics 1984, 16, 317.
9. Karlsson, R. J. Chem. Eng. Data 1973, 18, 290.
10. Roddy, J. W.; Coleman, C. F. Talanta 1968, 15, 1281.
11. Moule, D. C.; Thurston, W. M. Can. J. Chem. 1966, 44, 1361.
12. Schatzberg, P. J. Phys. Chem. 1963, 67, 776.
13. Selected Values of Properties of Hydrocarbons and Related Compounds. API Research Project 44, Thermodynamic Research Center, Department of Chemistry, Texas A & M University, College Station, Texas, 1970.
14. Franks, F.; Quickenden, M. A. J.; Reid, D. S. Nature 1969, 224, 1293.
15. De Lisi, R.; Goffredi, M.; Turco Liveri, V. J. Chem Soc. Faraday Trans. I 1980, 76, 1660.
16. Engdahl, A.; Nelander, B. J. Phys. Chem. 1985, 89, 2860.
17. Karlström, G.; Linse, P.; Wallqvist, A.; Jönsson, B. J. Am. Chem. Soc. 1983, 105, 3777.
18. Englin, B. A.; Plate, A. F.; Tugolukov, V. M.; Pryanishnikova, M.

A. Khim. i. Tekhnol. Topliv i Masel 1965, 10 (No. 9), 42; Chem.

Abstr. 1965, 63, 14608f.

TABLE 1. Results from experiments with benzene. $\Delta_{\text{sol}}H$ is the enthalpy of solution of water in the benzene sample and A is the integral from the g. c. determinations of the initial water content

T/K: 298.15		298.15		308.07	
$\Delta_{\text{sol}}H/\text{mJ}^{\text{a}}$	$A/(\text{mV}\cdot\text{s})^{\text{b}}$	$\Delta_{\text{sol}}H/\text{mJ}^{\text{c}}$	$A/(\text{mV}\cdot\text{s})^{\text{d}}$	$\Delta_{\text{sol}}H/\text{mJ}^{\text{c}}$	$A/(\text{mV}\cdot\text{s})^{\text{d}}$
15.24	2.94	31.35	26.7	47.33	8.16
15.17	2.80	23.38	68.6	46.09	11.0
10.62	8.26	6.11	156.7	39.63	38.4
9.90	9.58			17.17	133.2
4.78	16.2			15.74	140.1
3.56	17.5				

a 100 mm³ syringe; injection of 19.98 mm³.

b 100 mm³ syringe, injection of 2.76 mm³.

c 500 mm³ syringe; injection of 41.83 mm³.

d 500 mm³ syringe; injection of 27.88 mm³.

TABLE 2. Results from experiments with n-alkanes. $\Delta_{\text{sol}}H$ is the enthalpy of solution of water in the n-alkane sample and A is the integral from the g. c. determinations of the initial water content. A 500 mm³ syringe was used. 41.83 mm³ was injected into the calorimeter and 27.88 mm³ into the g. c. column

n-heptane ^a			n-octane ^a			n-decane ^a			n-decane ^b			n-dodecane ^a		
$\Delta_{\text{sol}}H/\text{mJ}$	$A/(\text{mV}\cdot\text{s})$	$\Delta_{\text{sol}}H/\text{mJ}$	$A/(\text{mV}\cdot\text{s})$	$\Delta_{\text{sol}}H/\text{mJ}$	$A/(\text{mV}\cdot\text{s})$	$\Delta_{\text{sol}}H/\text{mJ}$	$A/(\text{mV}\cdot\text{s})$	$\Delta_{\text{sol}}H/\text{mJ}$	$A/(\text{mV}\cdot\text{s})$	$\Delta_{\text{sol}}H/\text{mJ}$	$A/(\text{mV}\cdot\text{s})$	$\Delta_{\text{sol}}H/\text{mJ}$	$A/(\text{mV}\cdot\text{s})$	
4.07	3.32	2.68	2.54	4.00	1.44	6.82	3.34	3.29	1.60					
3.13	6.40	3.56	3.14	3.42	3.48	6.39	4.48	2.84	2.90					
2.26	9.32	3.47	3.94	3.18	4.08	6.12	5.08	2.54	3.34					
1.88	10.4	3.26	3.80	2.81	4.98	5.52	6.06	1.64	5.86					
0.98	14.3	3.10	3.94	2.07	7.40	4.54	8.62	0.13	9.80					
		3.06	4.14	1.20	9.60	3.84	9.92							
		2.74	5.64	1.17	10.2	3.76	10.2							
		1.76	8.26	0.26	12.9	3.18	11.6							
		0.97	10.6											
		0.46	11.8											
		0.20	13.0											

^a 298.15 K

^b 313.14 K

TABLE 3. Enthalpies and molar enthalpies for solution of water in some hydrocarbons at different temperatures. w is the mass fraction of water in the saturated hydrocarbon solution. The uncertainties given are estimates (see the text)

Solvent	T/K	$10^6 w$	$\Delta_{\text{sol}} H_{\text{int}}/\text{mJ}$	$\Delta_{\text{sol}} H_{\text{m}}/(\text{kJ}\cdot\text{mol}^{-1})$
benzene ^a	298.15	739 ^b	17.40 ± 0.42	24.3 ± 0.7
benzene	298.15	739 ^b	36.61 ± 0.55	24.4 ± 0.5
benzene	308.07	1017 ^c	48.92 ± 0.60	23.7 ± 0.5
n-heptane	298.15	91 ^d	4.95 ± 0.27	34.4 ± 2.3
n-octane	298.15	84 ^e	4.59 ± 0.23	33.6 ± 2.0
n-decane	298.15	72 ^d	4.51 ± 0.17	37.1 ± 1.9
n-decane	313.14	136 ^d	8.34 ± 0.33	36.3 ± 1.6
n-dodecane	298.15	65 ^d	3.90 ± 0.23	34.6 ± 2.4

^a From measurements with the 100 mm³ syringe.

^b Mean value from references 9 to 11.

^c Mean value from references 9 and 11

^d Reference 12

^e Interpolated value from reference 12.

LEGENDS

FIGURE 1. a, b, concentric glass tubes; c, brass tube; d, Wood's metal filling; e, brass cup containing the dissolution vessel; f, junction between the stainless steel tubes; g, stainless steel tube (i.d. 1.1 mm); h, stainless steel tube (i.d. 0.7 mm); i, n, calibration heaters; j, connection to solvent outlet from the reaction vessel; k, nozzle; l, brass tube; m, tin-soldered connection between the nozzle and the stainless steel tube.

FIGURE 2. Dissolution of water in benzene. Enthalpies of solution $\Delta_{\text{sol}}H$ against the integrals A from the initial water content determinations (see the text). ●, 100 mm³ syringe; injection of 19.98 mm³ into the calorimeter at 298.15 K and 2.76 mm³ into the g. c. 500 mm³ syringe; injection of 41.83 mm³ into the calorimeter and 27.88 mm³ into the g. c.; ■, at 298.15 K and ▲, at 308.07 K.

FIGURE 3. Dissolution of water in some n-alkanes. Enthalpies of solution $\Delta_{\text{sol}}H$ against the integrals A from the initial water content determinations (see the text). 500 mm³ syringe; injection of 41.83 mm³ into the calorimeter and 27.88 mm³ into the g. c. ■, n-decane at 313.14 K. ▲, n-heptane; ●, n-octane; □, n-decane; and ▼, n-dodecane at 298.15 K.

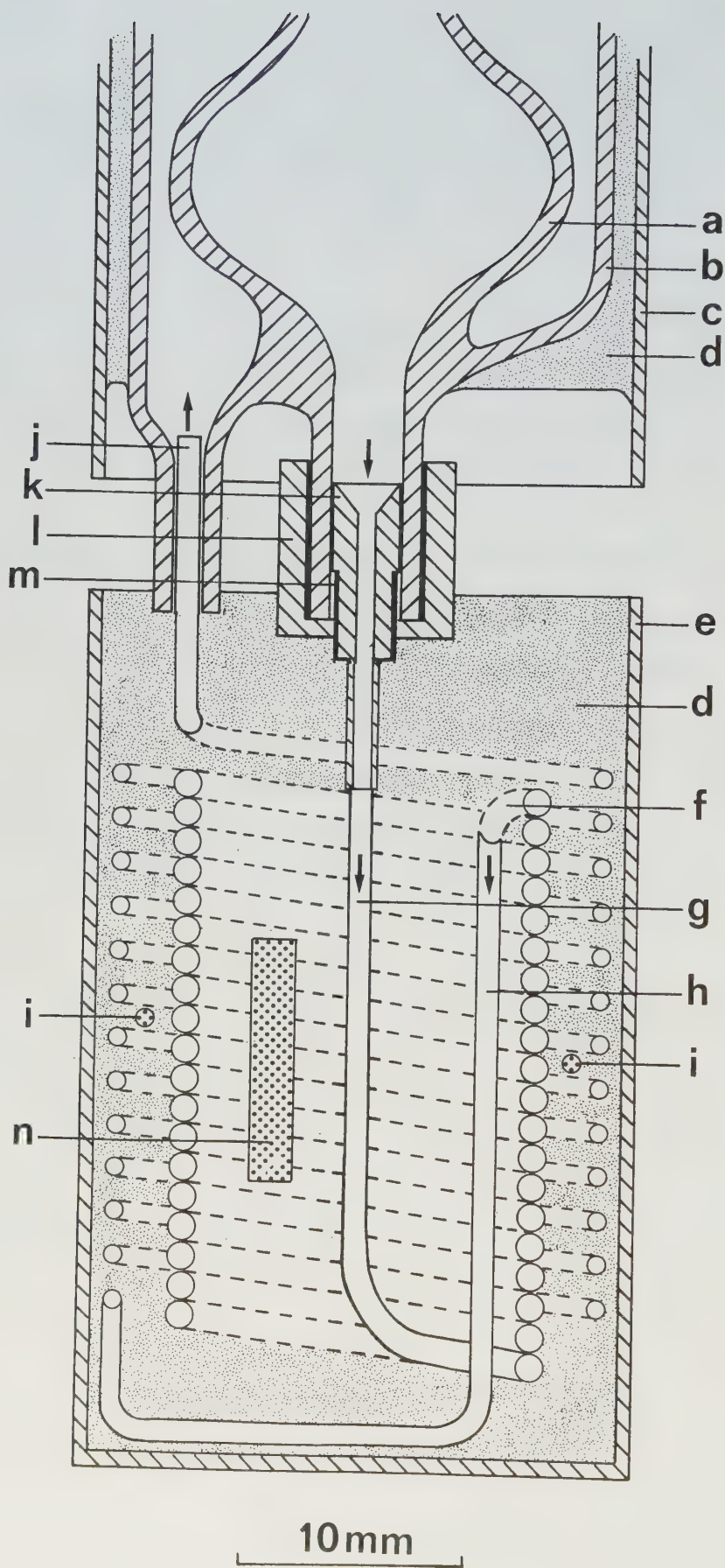


Figure 1

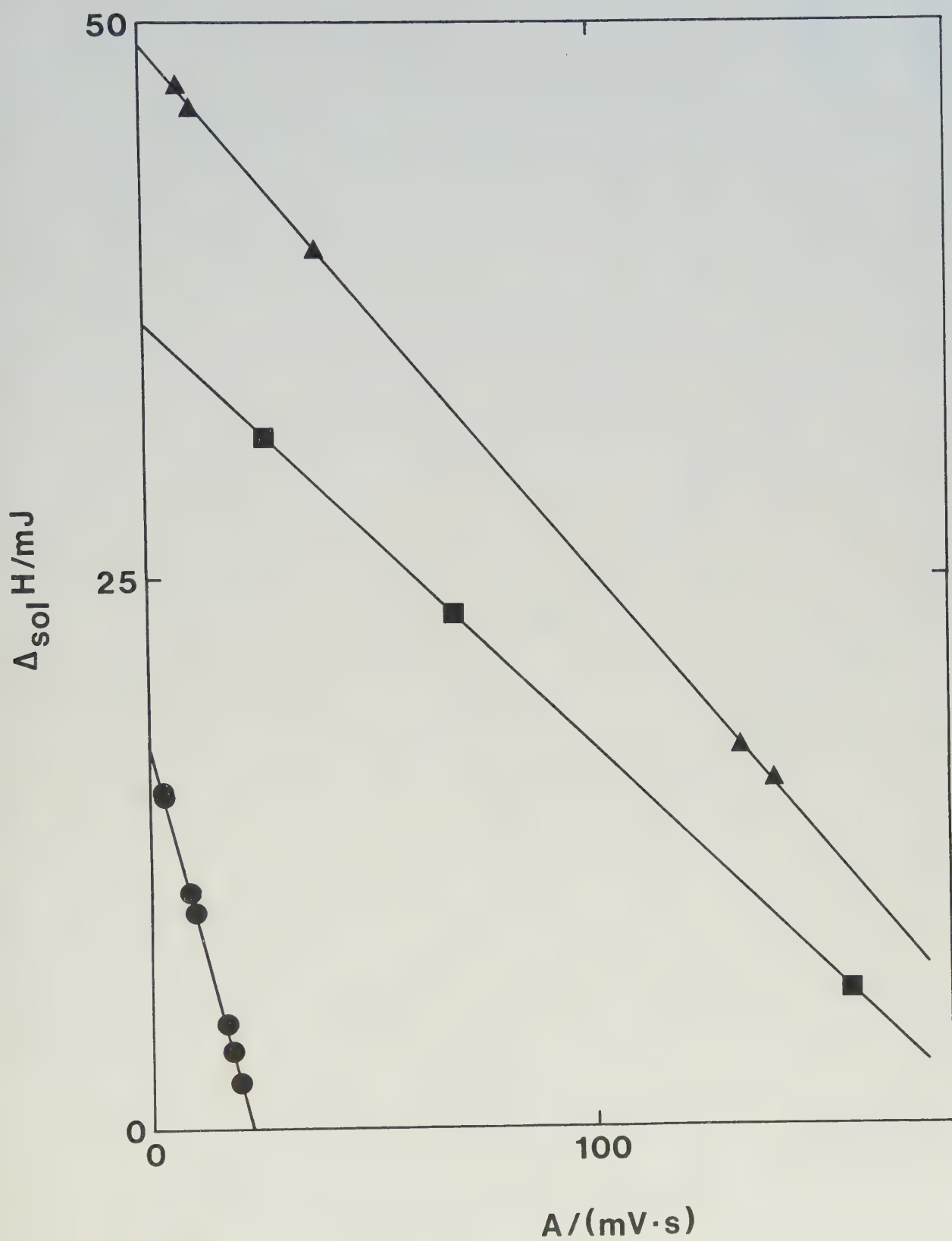


Figure 2

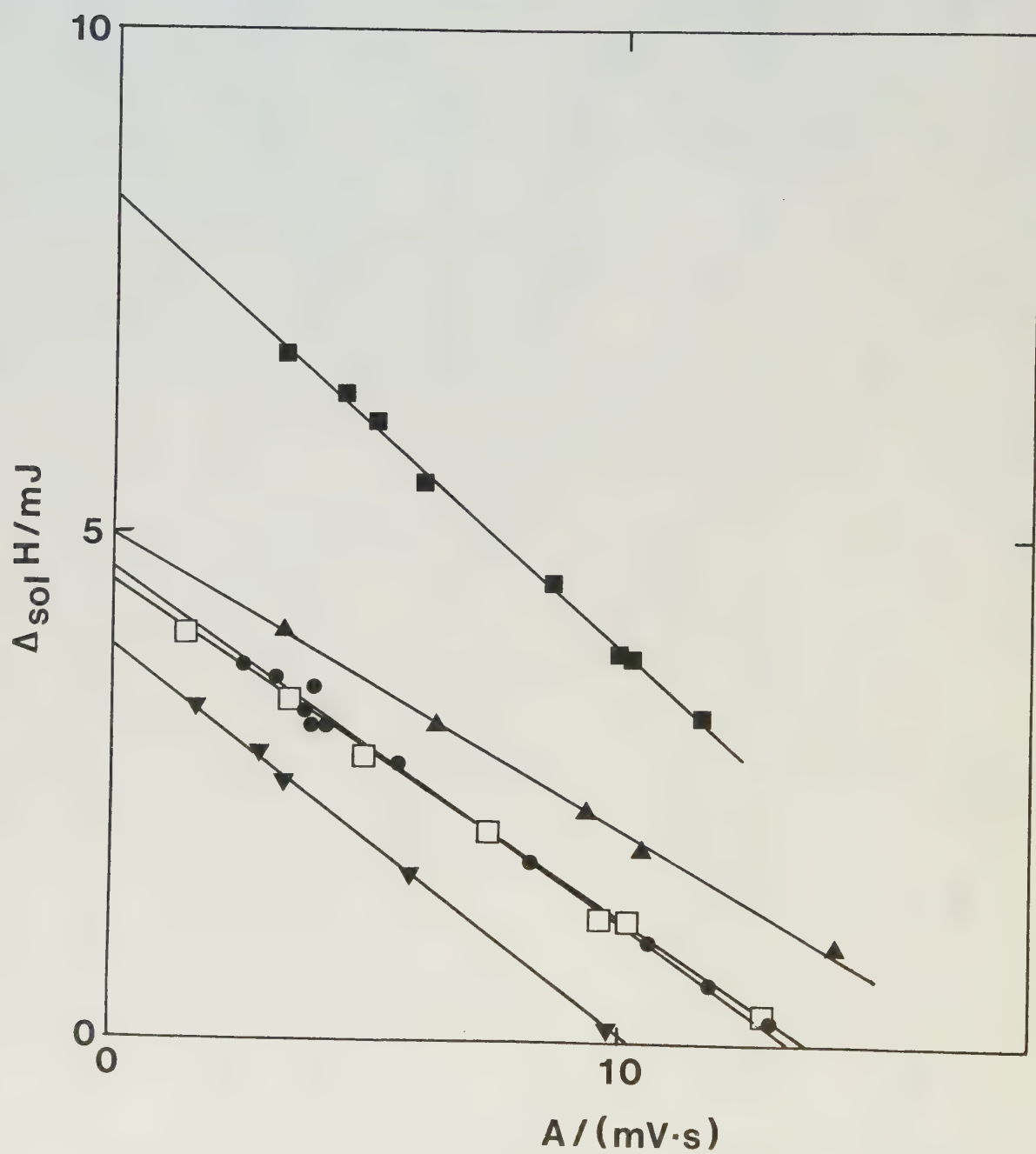


Figure 3

VI

Partial molar enthalpies of solution of water in some n-alkan-1-ols
and esters at 298.15 and 308.15 K

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Short title: Partial $\Delta_{\text{sol}}H_m$ of H_2O in alcohols and esters

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ABSTRACT

Partial molar enthalpies have been determined for dissolution of water in some n-alkan-1-ols (C_1 to C_8 , and C_{10}) and n-alkan-methylesters (C_3 , C_5 , C_7 , and C_9) and in ethyleneglycoldibutanoate and glycerol-tributanoate at 298.15 K. In addition, n-alkan-1-ols (C_3 and C_7), methylbutanoate and ethyleneglycoldibutanoate were measured at 308.15 K. The water molar fraction X_w was varied from very low values up to 0.04 to 0.1 for the alcohols and up to 0.03 to 0.06 for the esters. Coefficients are given for a polynomial fit of the enthalpies as a function of X_w .

1. Introduction

The present work is the second in a series of studies of the solution enthalpy for water in organic homologous series. Measurements on benzene and some n-alkanes were reported previously.⁽¹⁾ Here measurements on some n-alkan-1-ols and esters are presented.

In comparison with the hydrocarbons, the water solubility in these substances is much higher. This permitted an automatic technique in which small amounts of water were titrated into the sample. One of the advantages with this procedure is that the partial molar enthalpy of solution $\Delta_{\text{sol}}H_m(X_w)$ and the corresponding molar fraction X_w of water are obtained directly. The enthalpy of solution at infinite dilution $\Delta_{\text{sol}}H_m^\infty$ is obtained by extrapolating to $X_w = 0$.

The measurements were performed with a new microcalorimeter system^(2,3) developed in this laboratory.

2. Experimental

Methyloctanoate and methyldecanoate (Fluka AG puriss, better than 99 moles per cent by g. c.) were dried over 4A molecular sieves. n-Decan-1-ol (Fluka AG puriss, better than 99 moles per cent by g. c.) was used as received. For the other alcohols and esters investigated here, the samples used were the same as those described in references 4 and 5. The initial water contents of the samples are given in tables 1 and 3. Reagent-grade water produced by a Milli-Q filtration system was used.

A Varian 3700 g. c. was used to determine the water content. The column was packed with porapak Q 80 to 100 mesh and the hydrogen gas flow rate was $0.4 \text{ cm}^3 \cdot \text{s}^{-1}$. Benzene saturated with water was used as a calibration sample. Three mm^3 samples were injected.

The calorimetric dissolution experiments were performed by use of the prototype of the LKB BioActivity Monitor (a "4-channel" instrument, where each "channel" is a twin thermopile heat conduction calorimeter).⁽²⁾ A titration vessel fitted with a sample cup of 1 cm³ and a motor-driven stirrer⁽³⁾ were used. The sample cup was filled with 0.90 cm³ of the solvent. Water was introduced into the sample by use of a thin hypodermic needle (i.d. 0.15 mm) permanently fixed to a 100 mm³ gastight Hamilton syringe, positioned in a motor-driven syringe drive. Consecutive injections of about 0.8 to 1.8 mm³ of water were made at an injection rate of 0.003 mm³·s⁻¹. However, the first amount injected in all titration measurements is not well-defined. This leads to a larger scattering in the value for the first titration step. For some of the measurements, a small amount of water, about 0.17 mm³, was introduced into the sample as a first titration step. The heat effect observed was not taken into account, whereas the injected amount was added to the initial water content.

The integration time periods varied with the compounds and the water content at the time of the injection. For instance, methanol needed an integration period of 0.8 h, whereas n-decan-1-ol needed 2 h when the water content was very low and 5 h at a water molar fraction of 0.1.

Electrical calibrations were performed by use of an insertion heater positioned in the sample ampoule.

3. Results and discussion

After N titration steps, the mass $m_w(N)$ of water titrated into the sample is obtained by equation (1):

$$m_w(N) = N\rho_w(dV/dt)t, \quad (1)$$

where ρ_w is the density of water at the temperature 297.2 K of the syringe holder, $dV/dt = 0.002756 \text{ mm}^3 \cdot \text{s}^{-1}$ is the volume displacement rate, and t is the injection period. The molar fraction X_w of water is calculated from equation (2):

$$X_w = 1/(1 + M_w \rho_s V_s / M_s m_w), \quad (2)$$

where ρ_s and V_s are the solvent density and volume at room temperature 297 K and M_w and M_s are the molar masses for water and the solvent, respectively. Combining equations (1) and (2) gives equation (3), which shows the molar fraction $X_w(N)$ of water after N titration steps:

$$X_w(N) = 1/[1 + M_w/M_s \{m_{w,i}/\rho_s V_s + N\rho_w(dV/dt)t/\rho_s V_s\}], \quad (3)$$

where $m_{w,i}$ is the initial mass of water in the sample. The initial mass fraction w_i of water is small ($< 2 \times 10^{-3}$) and therefore $m_{w,i}/\rho_s V_s$ can be substituted by w_i .

During the N^{th} titration step, X_w changes from $X_w(N-1)$ to $X_w(N)$. For small changes the integral enthalpy value can be considered as the partial molar enthalpy of solution $\Delta_{\text{sol}} H_m(X_w)$ corresponding to the molar fraction $X_w(N-1/2)$ of water. This leads to equation (4):

$$X_w(N-1/2) = 1/[1 + M_w/M_s \{w_i + (N-1/2)\rho_w(dV/dt)t/\rho_s V_s\}] \quad (4)$$

Recently titration dissolution measurements of lower alcohols into a flow of water were reported.⁽⁶⁾ In these measurements a

significant diffusion at the tip of the hypodermic needle was observed. In the present measurements, where no solvent flow occurs, no such effect was seen.

Molar enthalpies of solution were obtained by equation (5):

$$\Delta_{\text{sol}}H_m = - \epsilon A M_w / \rho_w (dV/dt) t, \quad (5)$$

where ϵ is the calibration constant and A is the voltage-time integral recorded by the calorimeter. Densities were taken from references 5 and 7.

Table 1 shows the corresponding X_w and $\Delta_{\text{sol}}H_m(X_w)$ for dissolution of water in some n-alkan-1-ols and esters at 298.15 K. The results are mean values from three to four series of measurements. The table also shows w_i and t . $\Delta_{\text{sol}}H_m(X_w)$ is plotted against X_w for the alcohols in figure 1 and for the esters in figure 2. The enthalpy values are fitted to a quadratic or, in some cases, a linear equation as a function of X_w :

$$\Delta_{\text{sol}}H_m(X_w) = a + bX_w + cX_w^2 \quad (6)$$

Table 2 shows the coefficients, where $a = \Delta_{\text{sol}}H_m^\infty$.

Christensen et al.⁽⁸⁾ have summarized molar excess enthalpies $H_m^E(X_w)$ as a function of X_w , for some of the present solutions. Starting from:

$$\Delta_{\text{sol}}H_m(X_w) = H_m^E(X_w) + (1-X_w) \{ dH_m^E(X_w)/dX_w \}, \quad (7)$$

$H_m^E(X_w)$ is derived by equation (8):

$$H_m^E(X_w) = (1-X_w) \int_0^{X_w} \{\Delta_{sol} H_m(X_w)/(1-X_w)^2\} dX_w. \quad (8)$$

Combining equations (6) and (8) and integration lead to equation (9):

$$H_m^E(X_w) = (1-X_w) \{cX_w + (b+2c) \ln(1-X_w) + (a+b+c)X_w/(1-X_w)\}. \quad (9)$$

Figure 3 shows the excess enthalpy functions for C_1 to C_3 alcohols at 298.15 K derived from the present results by use of equation (9) and values reported in reference 8. The agreement with the literature values is good for methanol and ethanol with the exception of the results for ethanol by Lama R. F. et al.⁽⁸⁾ In comparison with results for propan-1-ol by Belousov V. P. et al.⁽⁸⁾ a systematic deviation is seen. Bertrand et al.⁽⁹⁾ have reported $\Delta_{sol} H_m^\infty$ at 298.15 K for methanol $-(3.01 \pm 0.02) \text{ kJ}\cdot\text{mol}^{-1}$ and ethanol $-(1.92 \pm 0.02) \text{ kJ}\cdot\text{mol}^{-1}$. The former value agrees well with the present result $-(2.99 \pm 0.04) \text{ kJ}\cdot\text{mol}^{-1}$, while the latter value is slightly less negative than our result $-(2.01 \pm 0.04) \text{ kJ}\cdot\text{mol}^{-1}$. No values have been found in literature for the higher alcohols or for the esters.

Figure 4 shows a plot of $\Delta_{sol} H_m^\infty$ against the number N_c of alkyl carbon atoms. The enthalpies increase with increasing alkyl chain length for the alcohols as well as for the methylesters and an essentially constant value of about $3.3 \text{ kJ}\cdot\text{mol}^{-1}$ is obtained for the alcohols (C_7 to C_{10}). Methylbutanoate, ethyleneglycoldibutanoate and glyceroltributanoate have identical ratios N_c/N_F , where N_F is the number of functional groups. It is interesting to note that values are within uncertainty limits identical as seen in figure 5.

Liquid alcohols and liquid water are extensively associated by

hydrogen bonding,⁽¹⁰⁻¹³⁾ whereas no hydrogen bonding can be expected in liquid esters. Addition of water to the pure alcohols will break hydrogen bonds in the alcohols as well as in the water, and water-alcohol aggregates will be formed. These aggregates seem to have different structures depending on the alcohol. D'Aprano et al.⁽¹⁴⁾ have measured dielectric constants of different alcohol solutions at low water content. They conclude that most of the water initially added to the lower alcohols forms chain polymers with the alcohols, while for n-pentan-1-ol and higher alcohols, most of the added water molecules serve as a nuclei for $H_2O(ROH)_4$ complexes. The $\Delta_{sol}H_m(X_w)$ values for the alcohols, shown in figure 1, thus appear to be due to very complex processes. Preliminary measurements on propan-1-ol and n-butan-1-ol over a larger concentration range (not reported in detail here) show maximum $\Delta_{sol}H_m(X_w)$ of X_w equal to 0.13 and 0.065, respectively.

Tables 3 and 4 show the results from measurements on a few alcohols and esters at 308.15 K. $\Delta_{sol}C_{p,m}^\infty$ values were derived from the temperature dependence of $\Delta_{sol}H_m^\infty$, table 5. The same values were found for propan-1-ol and n-heptan-1-ol. For the esters the values are close to zero.

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REFERENCES

1. Nilsson, S.-O. J. Chem. Thermodynamics, submitted
2. Suurkuusk, J.; Wadsö, I. *Chemica Scripta* 1982, 20, 155.
3. Görman Nordmark, M.; Laynez, J.; Schön, A.; Suurkuusk, J.; Wadsö, I. J. *Biochem. Biophys. Methods* 1984, 10, 187.
4. Hallén, D.; Nilsson, S.-O.; Rothschild, W.; Wadsö, I. J. Chem. Thermodynamics, in press.
5. Nilsson, S.-O.; Wadsö, I. J. Chem. Thermodynamics, in press.
6. Nilsson, S.-O.; Wadsö, I. J. Chem. Thermodynamics 1984, 16, 317.
7. Selected Values of Properties of Hydrocarbons and Related Compounds. API Research project 44, Thermodynamic Research Center, Department of Chemistry, Texas A & M University, College Station, Texas 1970.
8. Christensen, J.; Gmeling, J.; Rasmussen, P.; Weidlich, U. Heats of mixing. Data Collection, Binary Systems, Chemistry Data Series, Vol. III, Part 1. Schön and Wetzels: Frankfurt/Main. 1984.
9. Bertrand, G. L.; Millero, F. J.; Wu, C.; Hepler, L.G. J. Phys. Chem. 1966, 70, 699.
10. Franks, F.; Ives, D. J. G. Q. Rev. Chem. Soc. 1966, 20, 1.
11. Jorgensen, W. L. J. Am. Chem. Soc. 1981, 103, 341.
12. Jorgensen, W. L. J. Am. Chem. Soc. 1981, 103, 345.
13. Chandrasekhar, J.; Impey, R. W.; Jorgensen, W. L.; Klein, M. L.; Madura, J. D. J. Chem. Phys. 1983, 79, 926.
14. D'Aprano, A.; Caponetti, E.; Donato, D. I. J. Solution Chem. 1979, 8, 135.

TABLE 1. Partial molar enthalpies of solution $\Delta_{\text{sol}}H_m(X_m)$ of water in some alcohols and esters at 298.15 K, and the corresponding molar fractions X_w of water. N is the number of titration steps, w_i is the initial mass fraction of water and t is the injection period

methanol					ethanol				
$w_i = 5.5 \times 10^{-4}$ t = 300 s					$w_i = 2.5 \times 10^{-4}$ t = 420 s				
N	X_w	$\frac{\Delta_{\text{sol}}H_m(X_w)}{\text{kJ}\cdot\text{mol}^{-1}}$	N	X_w	$\frac{\Delta_{\text{sol}}H_m(X_w)}{\text{kJ}\cdot\text{mol}^{-1}}$	N	X_w	$\frac{\Delta_{\text{sol}}H_m(X_w)}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta_{\text{sol}}H_m(X_w)}{\text{kJ}\cdot\text{mol}^{-1}}$
1	0.0020	-2.98	11	0.0222	-2.80	1	0.0027	-1.98	-1.46
2	0.0041	-2.95	12	0.0242	-2.78	2	0.0069	-1.91	-1.43
3	0.0061	-2.95	13	0.0261	-2.74	3	0.0110	-1.83	-1.39
4	0.0082	-2.94	14	0.0281	-2.75	4	0.0150	-1.80	-1.36
5	0.0102	-2.88	15	0.0300	-2.72	5	0.0191	-1.74	-1.32
6	0.0122	-2.90	16	0.0320	-2.71	6	0.0231	-1.69	-1.28
7	0.0142	-2.83	17	0.0339	-2.69	7	0.0270	-1.63	
8	0.0162	-2.85	18	0.0359	-2.70	8	0.0310	-1.59	
9	0.0182	-2.82	19	0.0378	-2.68	9	0.0349	-1.56	
10	0.0202	-2.83	20	0.0397	-2.67	10	0.0388	-1.51	

cont.-

TABLE 1 cont.

propan-1-ol			n-butan-1-ol			n-pentan-1-ol		
$w_i = 3.1 \times 10^{-4}$ $t = 420$ s			$w_i = 17.6 \times 10^{-4}$ $t = 420$ s			$w_i = 5.9 \times 10^{-4}$ $t = 300$ s		
N	X_w	$\frac{\Delta_{sol} H_m(X_w)}{kJ \cdot mol^{-1}}$	N	X_w	$\frac{\Delta_{sol} H_m(X_w)}{kJ \cdot mol^{-1}}$	N	X_w	$\frac{\Delta_{sol} H_m(X_w)}{kJ \cdot mol^{-1}}$
1	0.0037	0.25	11	0.0541	0.67	1	0.0104	1.75
2	0.0090	0.29	12	0.0589	0.72	2	0.0168	1.78
3	0.0142	0.34	13	0.0636	0.72	3	0.0231	1.82
4	0.0194	0.40	14	0.0683	0.74	4	0.0293	1.84
5	0.0245	0.46	15	0.0729	0.76	5	0.0354	1.85
6	0.0296	0.49				6	0.0415	1.86
7	0.0346	0.54				7	0.0475	1.87
8	0.0395	0.58				8	0.0534	1.88
9	0.0444	0.61				9	0.0475	2.56
10	0.0493	0.65				10	0.0525	2.53
						11	0.0574	2.50

TABLE 1 cont.

n-hexan-1-ol					n-heptan-1-ol														
$w_i = 12.6 \times 10^{-4}$					$w_i = 1.3 \times 10^{-4}$					$w_i = 1.5 \times 10^{-4}$									
$t = 300$ s					$t = 420$ s					$t = 420$ s					$t = 660$ s				
N	X_w	$\frac{\Delta_{sol} H_m(X_w)}{kJ \cdot mol^{-1}}$	N	X_w	$\frac{\Delta_{sol} H_m(X_w)}{kJ \cdot mol^{-1}}$	N	X_w	$\frac{\Delta_{sol} H_m(X_w)}{kJ \cdot mol^{-1}}$	N	X_w	$\frac{\Delta_{sol} H_m(X_w)}{kJ \cdot mol^{-1}}$	N	X_w	$\frac{\Delta_{sol} H_m(X_w)}{kJ \cdot mol^{-1}}$					
1	0.0102	3.02	1	0.0052	2.99	1	0.0060	3.39	1	0.0088	3.36								
2	0.0164	3.02	2	0.0139	2.98	2	0.0158	3.26	2	0.0242	3.14								
3	0.0225	2.96	3	0.0225	2.93	3	0.0255	3.14	3	0.0391	2.98								
4	0.0286	2.92	4	0.0309	2.88	4	0.0350	3.06	4	0.0535	2.86								
5	0.0345	2.89	5	0.0392	2.83	5	0.0444	2.93	5	0.0675	2.74								
6	0.0404	2.82	6	0.0474	2.77				6	0.0811	2.62								
7	0.0464	2.81	7	0.0554	2.71				7	0.0944	2.49								
8	0.0520	2.73	8	0.0633	2.65														
9	0.0577	2.69	9	0.0711	2.59														
10	0.0633	2.66																	
11	0.0689	2.60																	

cont.-

TABLE 1 cont.

methylhexanoate				methyloctanoate				methyldecanoate				ethyleneglycoldibutanoate				glyceroltributanoate			
$w_i = 1.8 \times 10^{-4}$ $t = 300$ s				$w_i = 2.5 \times 10^{-4}$ $t = 300$ s				$w_i = 2.4 \times 10^{-4}$ $t = 300$ s				$w_i = 1.9 \times 10^{-4}$ $t = 300$ s				$w_i = 4.8 \times 10^{-4}$ $t = 300$ s			
N	X_w	$\frac{\Delta_{sol} H_m(X_w)}{kJ \cdot mol^{-1}}$		N	X_w	$\frac{\Delta_{sol} H_m(X_w)}{kJ \cdot mol^{-1}}$		N	X_w	$\frac{\Delta_{sol} H_m(X_w)}{kJ \cdot mol^{-1}}$		N	X_w	$\frac{\Delta_{sol} H_m(X_w)}{kJ \cdot mol^{-1}}$		N	X_w	$\frac{\Delta_{sol} H_m(X_w)}{kJ \cdot mol^{-1}}$	
1	0.0050	11.02		1	0.0068	11.85		1	0.0079	11.9		1	0.0073	9.54		1	0.0154	9.51	
2	0.0124	10.76		2	0.0158	11.28		2	0.0185	10.5		2	0.0173	9.46		2	0.0297	9.21	
3	0.0197	10.47		3	0.0247	10.71		3	0.0290	8.3		3	0.0272	9.05		3	0.0435	8.90	
4	0.0269	10.00		4	0.0334	9.60						4	0.0369	8.72		4	0.0570	8.49	
5	0.0340	9.49										5	0.0464	8.47					
												6	0.0557	8.15					

TABLE 2. Coefficients of equation (6) and molar enthalpies of solution

$\Delta_{\text{sol}}H_m^\infty$ of water at infinite dilution at 298.15 K. Uncertainties are twice the standard deviation of the mean.

Solvent	a/(kJ·mol ⁻¹)	b/(kJ·mol ⁻¹)	c/(kJ·mol ⁻¹)	$\frac{\Delta_{\text{sol}}H_m^\infty}{\text{kJ·mol}^{-1}}$ ^e
CH ₃ OH ^d	-2.99 $\pm$ 0.02	8.4 $\pm$ 0.7	-	-2.99 $\pm$ 0.04
C ₂ H ₅ OH	-2.01 $\pm$ 0.03	15.2 $\pm$ 1.0	-56 $\pm$ 15	-2.01 $\pm$ 0.04
C ₃ H ₇ OH	0.20 $\pm$ 0.02	11.9 $\pm$ 0.8	-57 $\pm$ 10	0.20 $\pm$ 0.02
C ₄ H ₉ OH	1.68 $\pm$ 0.03	7.1 $\pm$ 1.4	-65 $\pm$ 11	1.68 $\pm$ 0.04
C ₅ H ₁₁ OH	2.66 $\pm$ 0.02	-0.3 $\pm$ 1.2	-41 $\pm$ 14	2.66 $\pm$ 0.04
C ₆ H ₁₃ OH	3.05 $\pm$ 0.05	-3.5 $\pm$ 1.9	-43 $\pm$ 24	3.05 $\pm$ 0.06
C ₇ H ₁₅ OH ^d	3.41 $\pm$ 0.04	-10.0 $\pm$ 0.7	-	3.41 $\pm$ 0.06
C ₈ H ₁₇ OH ^d	3.31 $\pm$ 0.03	-12.1 $\pm$ 0.5		3.31 $\pm$ 0.05
C ₁₀ H ₂₁ OH	3.24 $\pm$ 0.05	-21.8 $\pm$ 1.5	52 $\pm$ 12	3.24 $\pm$ 0.07
CH ₃ OCOC ₃ H ₇	9.95 $\pm$ 0.07	-37.7 $\pm$ 3.8	-376 $\pm$ 63	9.95 $\pm$ 0.13
C ₂ H ₄ (OCOC ₃ H ₇) ₂ ^d	9.86 $\pm$ 0.15	-30.2 $\pm$ 4.0	-	9.86 $\pm$ 0.18
C ₃ H ₅ (OCOC ₃ H ₇) ₃ ^d	9.92 $\pm$ 0.13	-24.3 $\pm$ 3.2	-	9.91 $\pm$ 0.20
CH ₃ OCOC ₅ H ₁₁	11.11 $\pm$ 0.08	-14.6 $\pm$ 8.3	-974 $\pm$ 207	11.11 $\pm$ 0.14
CH ₃ OCOC ₇ H ₁₅	11.98 $\pm$ 0.43	-11 $\pm$ 47	-1790 $\pm$ 1140	11.98 $\pm$ 0.47
CH ₃ OCOC ₉ H ₁₉	12.6	-55	-3220	12.6 $\pm$ 0.8 ^f

^d Linear regression

^e Uncertainties given include estimates for systematic errors due to calibrations and impurities.

^f The uncertainty is an estimate.

TABLE 3. Partial molar enthalpies of solution $\Delta_{sol}H_m(X_w)$ of water in some alcohols and esters at 308.15 K, and the corresponding molar fraction X_w of water. N is the number of titration steps, w_i is the initial mass fraction of water and t is the injection period.

propan-1-ol						n-heptan-1-ol		
$w_i = 4.9 \times 10^{-4}$			$t = 420 \text{ s}$			$w_i = 3.7 \times 10^{-4}$		
N	X_w	$\frac{\Delta_{sol}H_m(X_w)}{\text{kJ}\cdot\text{mol}^{-1}}$	N	X_w	$\frac{\Delta_{sol}H_m(X_w)}{\text{kJ}\cdot\text{mol}^{-1}}$	N	X_w	$\frac{\Delta_{sol}H_m(X_w)}{\text{kJ}\cdot\text{mol}^{-1}}$
1	0.0043	0.89	11	0.0547	1.20	1	0.0074	3.96
2	0.0096	0.93	12	0.0594	1.22	2	0.0172	3.85
3	0.0148	0.97	13	0.0641	1.23	3	0.0269	3.72
4	0.0200	1.01	14	0.0688	1.24	4	0.0364	3.59
5	0.0251	1.05	15	0.0734	1.25	5	0.0457	3.48
6	0.0301	1.09	16	0.0780	1.26	6	0.0548	3.39
7	0.0351	1.12	17	0.0825	1.28	7	0.0637	3.27
8	0.0401	1.14	18	0.0870	1.28			
9	0.0450	1.16						
10	0.0498	1.19						

methylbutanoate						ethyleneglycoldibutanoate		
$w_i = 4.1 \times 10^{-4}$			$t = 300 \text{ s}$			$w_i = 3.7 \times 10^{-4}$		
N	X_w	$\frac{\Delta_{sol}H_m(X_w)}{\text{kJ}\cdot\text{mol}^{-1}}$	N	X_w	$\frac{\Delta_{sol}H_m(X_w)}{\text{kJ}\cdot\text{mol}^{-1}}$	N	X_w	$\frac{\Delta_{sol}H_m(X_w)}{\text{kJ}\cdot\text{mol}^{-1}}$
1	0.0052	9.62	9	0.0492	7.47	1	0.0092	9.77
2	0.0109	9.34	10	0.0544	7.22	2	0.0193	9.56
3	0.0166	8.98	11	0.0596	7.07	3	0.0291	9.38
4	0.0222	8.69				4	0.0388	8.86
5	0.0277	8.50				5	0.0482	8.70
6	0.0332	8.24				6	0.0575	8.37
7	0.0386	7.94				7	0.0666	8.12
8	0.0439	7.72						

TABLE 4. Coefficients of equation (6) and molar enthalpies of solution $\Delta_{\text{sol}}H_m^\infty$ of water at infinite dilution at 308.15 K. Uncertainties are twice the standard deviation of the mean.

Solvent	a/(kJ·mol ⁻¹)	b/(kJ·mol ⁻¹)	c/(kJ·mol ⁻¹)	$\frac{\Delta_{\text{sol}}H_m^\infty^e}{\text{kJ·mol}^{-1}}$
C ₃ H ₇ OH	0.85 $\pm$ 0.02	9.2 $\pm$ 0.5	-49 $\pm$ 5	0.85 $\pm$ 0.03
C ₇ H ₁₅ OH ^d	4.05 $\pm$ 0.02	12.3 $\pm$ 0.5	-	4.05 $\pm$ 0.05
CH ₃ OCOC ₃ H ₇	9.89 $\pm$ 0.10	-54.9 $\pm$ 5.0	118 $\pm$ 75	9.89 $\pm$ 0.15
C ₂ H ₄ (OCOC ₃ H ₇) ₂ ^d	10.11 $\pm$ 0.14	-29.9 $\pm$ 3.3	-	10.11 $\pm$ 0.18

^d Linear regression

^e Uncertainties given include estimates for systematical errors due to calibrations and impurities.

TABLE 5. $\Delta_{\text{sol}}C_{p,m}^{\infty}$ for the dissolution of water in some alcohols and esters for the temperature range 298.15 to 308.15 K.

Uncertainties are twice the standard deviation of the mean.

Solvent	$\Delta_{\text{sol}}C_{p,m}^{\infty}/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$
$\text{C}_3\text{H}_7\text{OH}$	65 ± 3
$\text{C}_7\text{H}_{15}\text{OH}$	64 ± 5
$\text{CH}_3\text{OCOC}_3\text{H}_7$	-6 ± 13
$\text{C}_2\text{H}_4(\text{OCOC}_3\text{H}_7)_2$	25 ± 21

FIGURE LEGENDS

FIGURE 1. Partial molar enthalpies of solution $\Delta_{\text{sol}}H_m(X_w)$ of water in some n-alkan-1-ols plotted against the molar fraction X_w of water at 298.15 K. ∇ , methanol; $\blacktriangledown$, ethanol; $+$, propan-1-ol; $\square$, n-butan-1-ol; $\blacksquare$, n-pentan-1-ol; $\blacktriangle$, n-hexan-1-ol; $\bullet$, n-heptan-1-ol; $\bigcirc$, n-octan-1-ol; and $\triangle$, n-decan-1-ol.

FIGURE 2. Partial molar enthalpies of solution $\Delta_{\text{sol}}H_m(X_w)$ of water in some esters plotted against the molar fraction X_w of water at 298.15 K. $\blacktriangledown$, methylbutanoate; $\blacksquare$, methylhexanoate; $\bullet$, methyloctanoate; $\square$, methyldecanoate; $\triangle$, ethyleneglycoldibutanoate; and $\bigcirc$, glyceroltributanoate.

FIGURE 3. Excess molar enthalpies for the binary system of water and alkan-1-ols (C_1 to C_3) at 298.15 K, plotted against the molar fraction X_w of water. The curves are derived from the present results by use of equation (9). Values for the points are taken from reference 8. Methanol: $\bullet$, Belousov V. P. et al. (1976). Ethanol: $\blacksquare$, Belousov V. P. et al. (1976); $\blacktriangledown$, Costigan M. J. et al. (1980); $\square$, Lama R. F. et al. (1965). Propan-1-ol: $\blacktriangle$, Belousov V. P. et al. (1976).

FIGURE 4. $\Delta_{\text{sol}}H_m^\infty$ for water in some n-alkan-1-ols and esters at 298.15 K plotted against the number N_c of alkyl carbon atoms. $\blacktriangledown$, n-alkan-1-ols; $\bullet$, methylesters; $\blacktriangle$, ethyleneglycoldibutanoate; $\blacksquare$, glyceroltributanoate.

FIGURE 5. $\Delta_{\text{sol}}H_m^\infty$ for water in some esters at 298.15 K plotted against the ratio N_c/N_f . N_c and N_f are the numbers of alkyl carbon atoms and the numbers of functional groups, respectively. $\bullet$, methylesters; $\blacktriangle$, ethyleneglycoldibutanoate; $\blacksquare$, glyceroltributanoate.

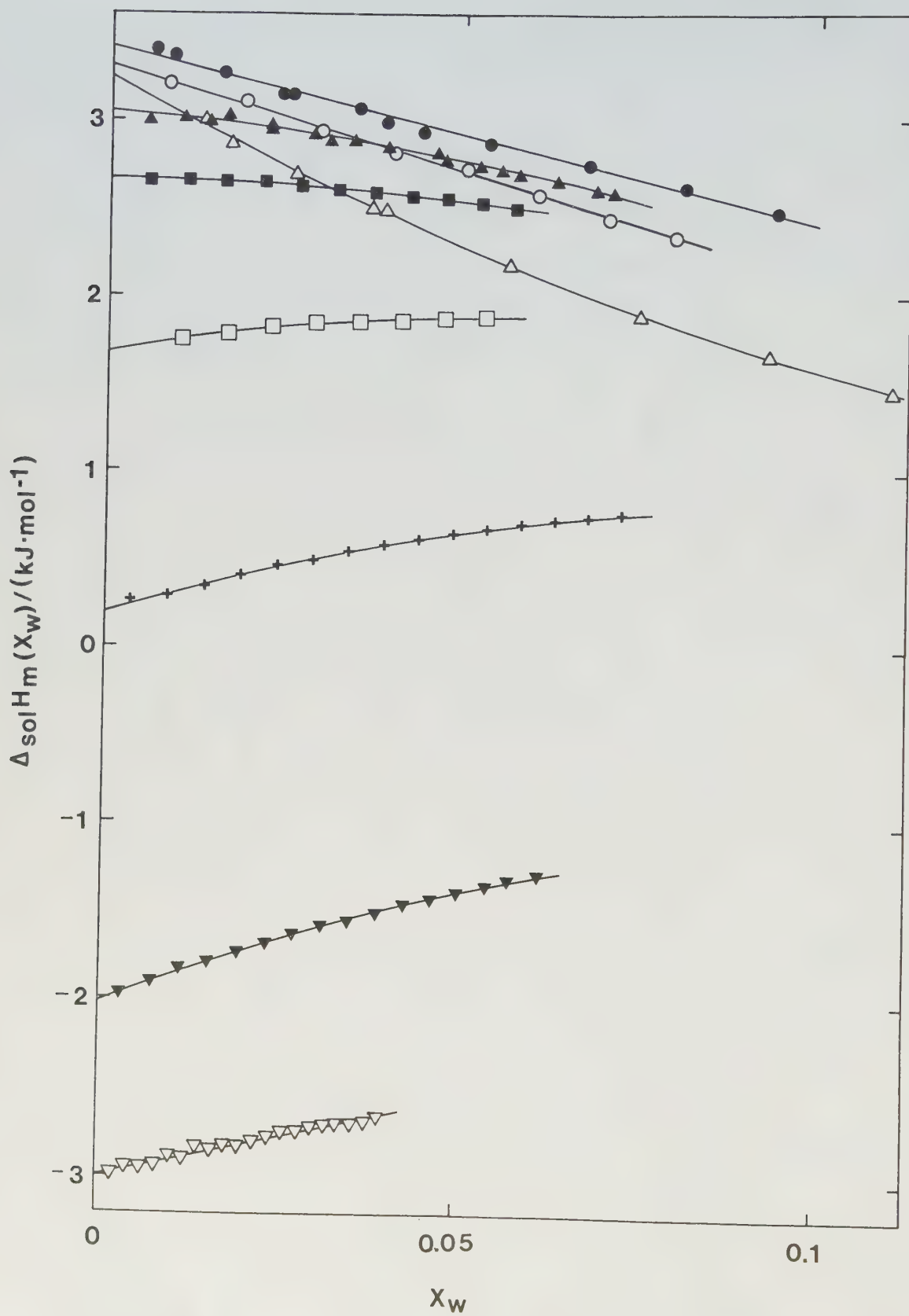


Figure 1

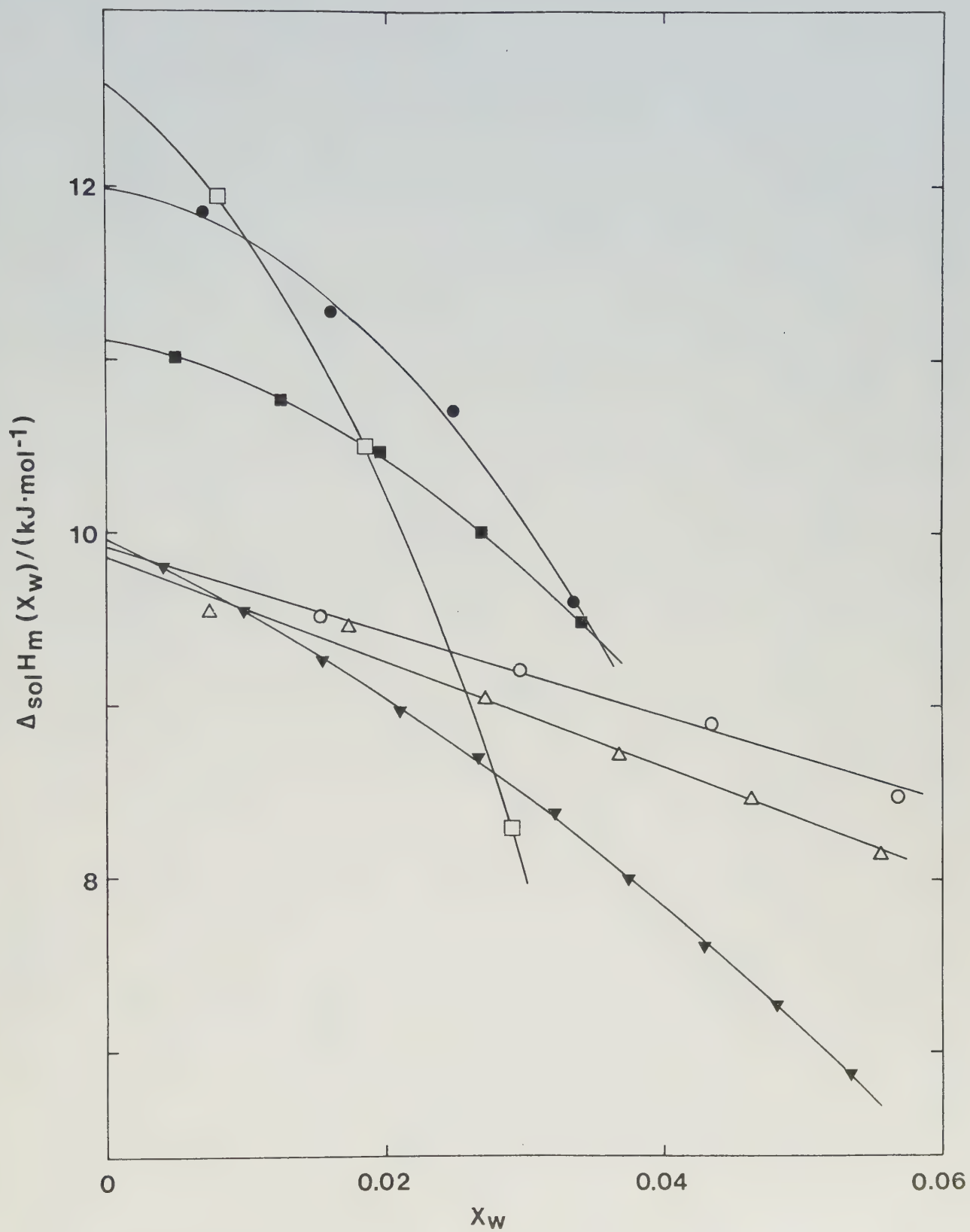


Figure 2

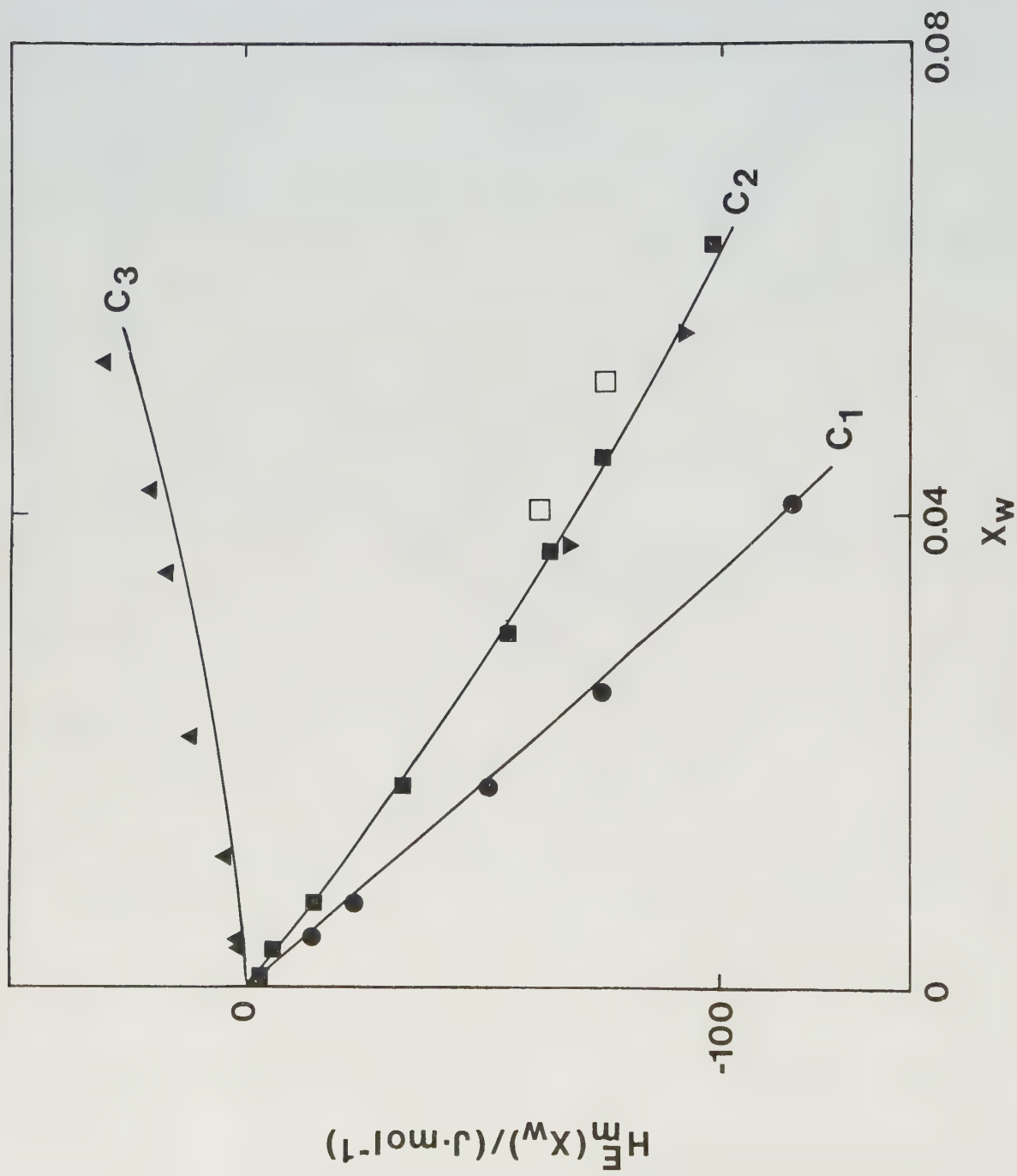


Figure 3

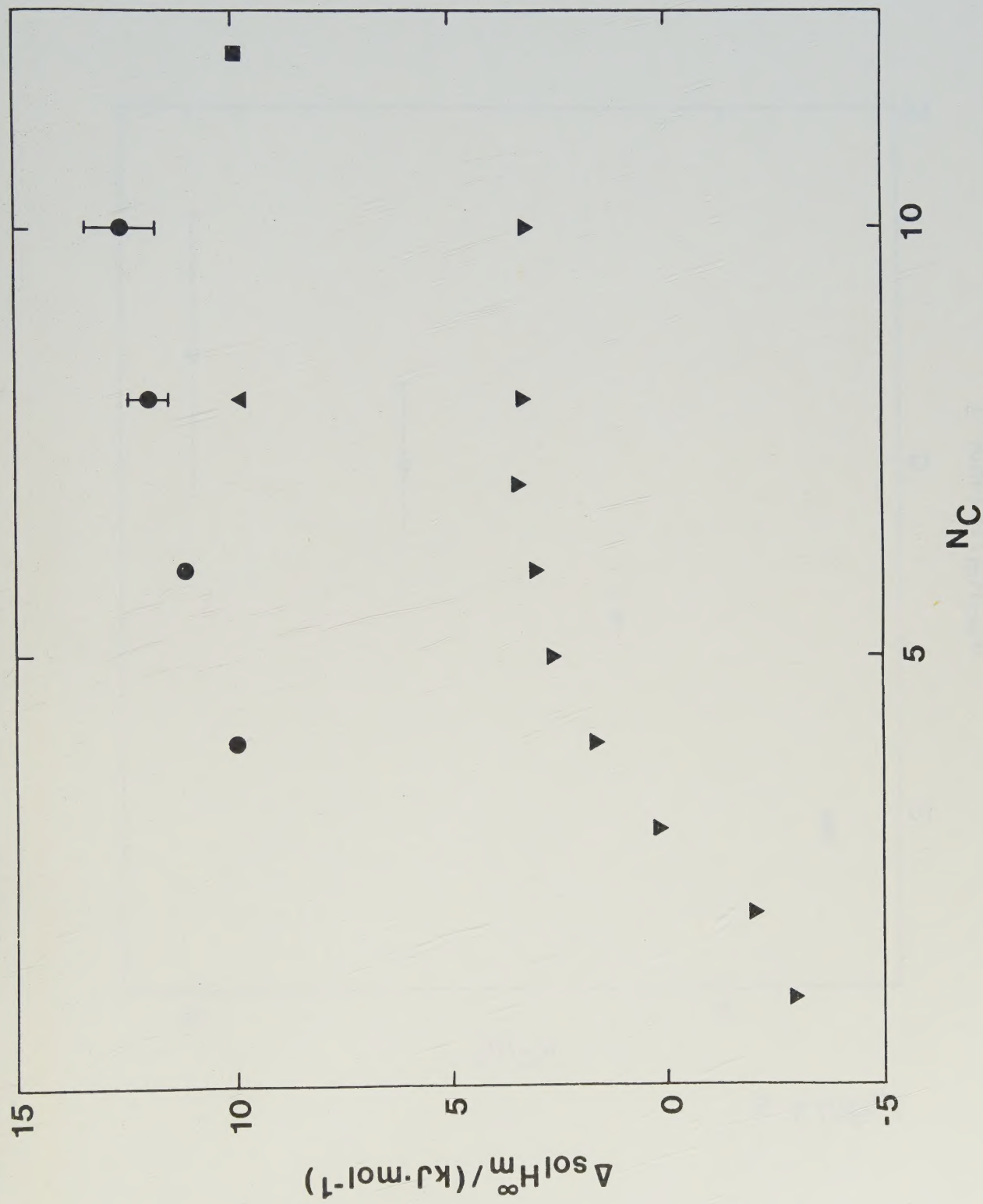


Figure 4

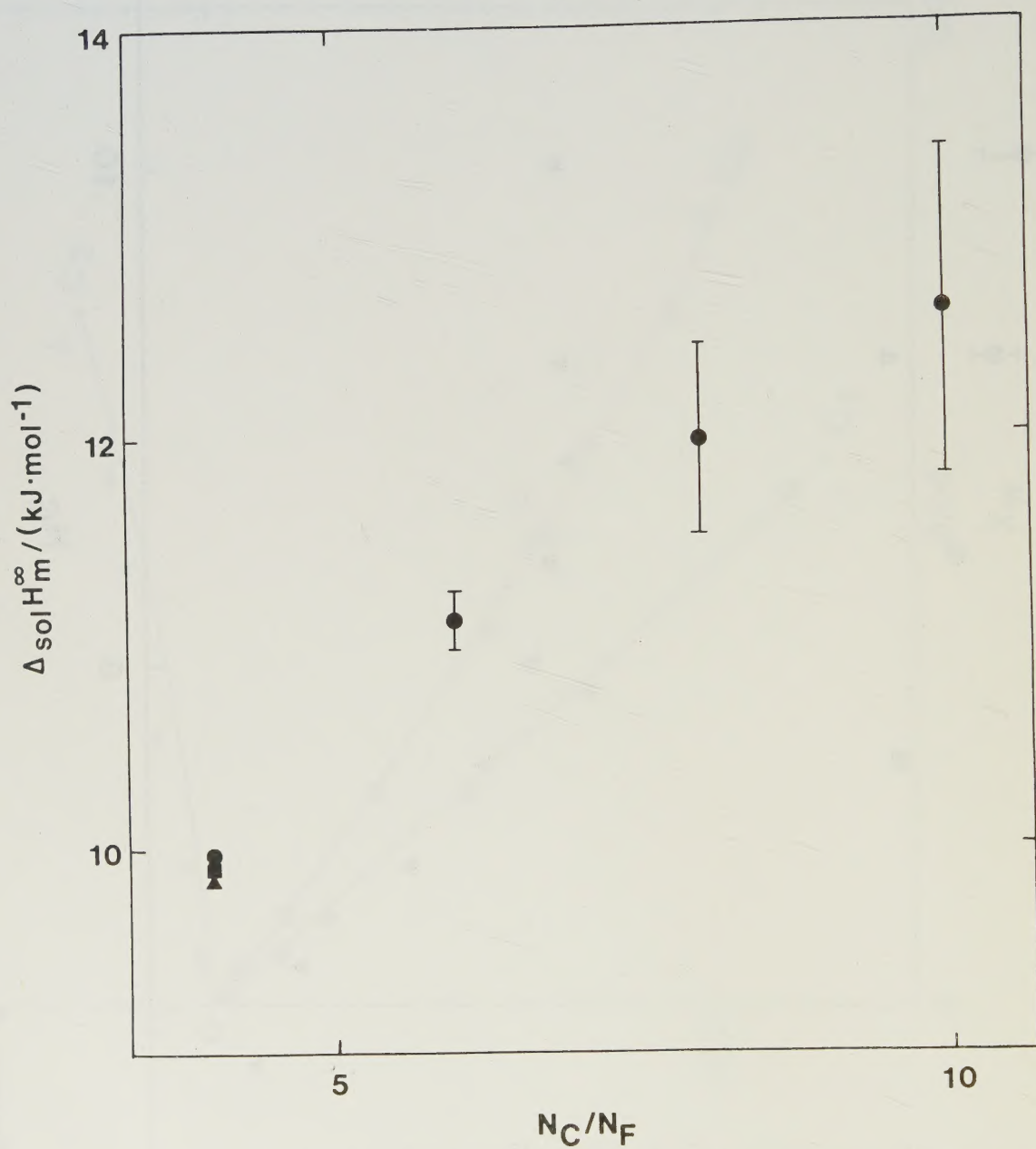


Figure 5

